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Abstract: Radioactive contaminated soil may arise due to accidents of various types or may be detected during decommissioning of nuclear installations. Ordinary surface soil cannot normally be conditioned using conventional cementation processes since the content of humic materials retards or prevents solidification. An additive available from the Danish firm Geodur A/S makes it possible to circumvent this difficulty and to produce a monolithic, nondusting waste type using rather small amounts of cement. The report describes work on characterization of such a cemented waste products prepared on basis of a clayey top soil from the Risø area.

The claimed advantages of the process was verified, and data for the compression strength (low), hydraulic conductivity (satisfactory) and other pore structure-related properties are given for the obtained products.

Unfortunately the behaviour of cesium and strontium, representing two of the most relevant radionuclides, was not too promising.

The retention of cesium is satisfactory, but less good than for the untreated soil. Greatly improved cesium retention after drying of the materials was noticed. Good retention of strontium is only obtained after reaction of the material with carbon dioxide from the atmosphere. The behaviour of the two isotopes in other types of cemented waste is somewhat similar, but the decrease in retention compared with untreated soil makes the process less interesting as a possibility for remedial actions after accidents, etc. Some further studies of the cemented soil waste are beeing made within the frame of the Nordic Nuclear Safety Studies.

Elements forming low solublity components in the high pH environment in the cemented soil will probably be retained quite efficiently. This was demonstrated in case of Zn.

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CONTENTS:

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1. Introduction

The safe handling and disposal of polluted soil is a special case of waste management. With some types of pollutants it may not be possible or economically feasible to remove the undesirable components, and permanent disposal of the soil could then be a desirable option. Soils contaminated with significant amounts of heavy metals or long-lived radioisotopes are obvious candidates for this route of management.

Radioactive contaminated soil may arise in connection with accidents in nuclear installations or during transport of radioactive materials. Contaminated soil may also be detected during decommisioning of nuclear installations.

The contaminated soil may of course be disposed of as such in suitable disposal facilities, but it is also of interest to investigate whether modification of the soil properties under certain circumstances may result in improved or less costly possibilities for disposal.

The danish firm GEODUR A/S has developed an additive which makes it possible to overcome the retardation effects which prevents normal hardening of cement/soil mixtures. Monolithic blocks with very low cement contents (~8 %) and an adequate strength can be made. This was demonstrated by the firm in december 1988 using top soil from the Risø area.

The process was thought to be of interest for practical waste management at Risø, where a considerable amount of soil contaminated with ^{90}Sr, at a low but still significant level, was used years ago to study Sr uptake in plants. The contaminated soil is presently in storage, but since it is planned to move the material, a conditioning should be considered.

The quality of the GEODUR product in such a context was undocumented and it has therefore been necessary to make an experimental study of the product. Results from this investigation are presented in the following.

Part of the material - together with results from other studies of GEODUR products made by the Danish Water Quality Institute /1/ - was presented at the 2. International Symposium on 'Stabilization/Solidification of Harzadous, Radioactive, and Mixed Waste' at Williamsbourg, Virginia, May/June 1990 /2/.

Further studies of GEODUR/cement-solidified soils has been done under the new Internordic NKS projects 1990-93 concerned with aspects of nuclear safety and financed by the Nordic nuclear safety authorities /3/. The relevant project is KAN 2: 'Avfallshantering vid markbelägning, olyckshändelser, transport av radioaktivt material m.m'. The present report can be regarded as a prequalification study for the Nordic project, but some of the results from these later experiments are used in the report for comparative purposes.

Sections 2 to 7 contain a detailed presentation of the experimental work on GEODUR products made at Risø before the Nordic study was initiated. A summary and recommendations for further work are given in Section 8.

2. Sample preparation

In september 1989 four different cemented products were prepared from surface soil and Danish sulphate resistant Portland cement (SRPC). Various amounts of cement and the GEODUR additive were employed. One of the products was made without the additive. Similar inactive products and products contaminated by radioisotopes were prepared. Later a few additional inactive samples with decreased water content have also been made.

2.1. Materials

The soil was obtained from a store of top soil maintained by the agricultural department at Risø. It has been collected from the tillage layer of fields in the area. The soil was sieved (< 5 mm) and homogenized.

Soil from the same store has been characterized in connection with previous soil chemistry studies (unpublished). It is developed from typical moraine material and is classified as a sandy clay. A typical texture analysis is given in Table 2.

The loss on ignition (2 hours at 800°C) was found to be 4.3 % representing the content of organics and some water loss from the clay.

The soil pH is ~7.3 (10 g soil in 25 ml 0.01 M $CaCl_2$).

At pH ~7 the cation-exchange capacity: CEC is ~18 meq/100 g soil and at pH 8.2 the CEC = 22.3 meq/100 g. Some further increase may be expected with increasing pH but this has not been investigated.

The pH-dependent part of the capacity is (partly) due to the content of organics in the soil. With decreasing pH further decreases in the variable capacity is taking place leaving - at pH < ~3 - only a permanent capacity of about 9 meq/100 g associated with the clay particles.

In the highly alkaline environment in a GEODUR product the CEC of the embedded soil will be high and the sites are probably mainly covered by Ca^{2+} ions. The ion-exchange properties may be important for the understanding of retention of minor components in the material.

The results of analyses of acid extracts of a sample of the soil are given in Table 3. Only reasonably easily extractable materials is dissolved by the treatment, mainly the amounts associated with the ion-exchange sites. Much higher contents especially of the alkali metals are bound in more or less unattacked silicates in the mineral grains in the soil.

Table 1. Texture of homogenized surface soil from the store at Risø agricultural department.

	Humus	Clay <0.002 mm	Silt 0.002-0.02	Fine sand 0.02-0.2	Coarse sand 0.2 - 2 mm
%	2.1	13	17	46	24

Table 2. Major acid extractable components in the soil (2 hours' shaking of 5 g soil with 50 ml 0.1 N HCl, final pH 1.65) and typical composition of sulphate resistant Portland cement.

	K	Na	Mg	Ca	Sr	Zn
	mg/g of dry soil or SRPC					
Found in acid extract of soil	0.13	0.04	0.16	3.7	-	0.006
SRPC (total)	1.6	1.1	5.2	540	1.6	-

The cement was ordinary sulphate resistant Portland cement (SRPC) from Aalborg Portland cement factories. This type of cement is made without fly ash, which otherwise is used extensively as a component in Danish cement products. Analyses of (another batch) of similar material gave compositions as indicated in Table 2.

The GEODUR additive is a white milky liquid containing 1 % of materials with unspecified composition. The liquid was prepared and delivered by GEODUR aps. It is certified to be non-toxic.

Tracers and additional carriers in form of ^{134}Cs, ^{85}Sr, ^{65}Zn and inactive CsCl, $SrCl_2$ and $ZnCl_2$ solutions were added to the active preparations.

2.2. Procedure.

The mixtures were made in batches of 3-4 kg in a stainless steel mixer with an excentric double-rotating stirrer. Each type was prepared in an inactive and an active version.

In case of the active products the soil was premixed in a semi-dry state (8.8-11.6 % moisture) for some minutes after addition of 20 ml solution containing the radioactive isotopes and the additional carriers.

The required amount of GEODUR liquid was then added and the mixing continued for about 3-5 minutes with the soil still in a more or less free-flowing semi-dry state. However, a sticky character due to the high clay content in the soil could be noticed.

The mixing was somewhat more easy after addition of the dry cement powder and was continued for an additional ~5 minutes.

Water was then added and the mixtures went through an extremely sticky state to a more soft but still claylike paste which could be blended reasonably easily. Unfortunately it had a rather undesirable rheology as far as casting was concerned. Although vibration was employed addition of more water than originally expected was needed to obtain castable mixtures.

Samples were cast from the inactive mixtures in form of small cylinders for compression-strength measurements (Section 3.1). Larger cylinders were cast in 500 ml polyethylen flasks. They were after hardening sectioned into disks for measurements of hydraulic permeability and diffusivities (Sections 4.1. and 6). Spherical samples fitted with a stainless steel-wire handle were cast in rubber moulds and later used in studies of leaching of cement components and volume stability under continuous leaching and under wet/dry cycling conditions (Section 5.3).

Samples were cast from the active mixture in form of 4 cm thick cylinders as a bottom layer in 500 ml polyethylen flasks and in polyethylene bags as flat plates which were later broken into pieces. Both types were used for leaching experiments (Sections 5.1 and 5.2).

The samples were hardened under high-humidity condition from one to two months before testing was initiated.

2.3. The types of mixtures.

The mixing proportions recommended by GEODUR aps are 8 % cement and 2 % GEODUR additive relative to the original amount of slightly moist soil (type No 1). This is partly founded on economical considerations but for radioactive waste conditioning minimizing the cement consumption may not be that important. A mixture (No. 2) with 16 % cement and 2 % GEODUR was therefore also prepared. The two last mixtures contain 8 % cement and 6 % or 0 % GEODUR, respectively (Nos. 3 and 4). The material without the additive can be regarded as a sort of reference.

Table 3. Recipies and composition of the cement products. The active and inactive products with same number are approximately identical except for the activity indicated by an A added to the number. The activities are given at Oct. the 23. 1989 at the beginning of the leaching period. Products 1A, 2A, 3A and 3 were made from soil with somewhat higher water content than the others.

Proportions GEODUR Cement	Recipie:	g	water g	Ca	K	Na	Cs	Sr	Zn	^{134}Cs	^{85}Sr	^{65}Zn
				mg						kBq		
2 %	Soil	3000	264	10100	350	110			16			
8 %	GEODUR	60	60									
	SRPC	200		129600	380	260		380				
	Water	600	600									
	Total:	3900	924	139700	730	370		380	16			
No. 1	Water content		23.7%	mg/g								
	w/c=		3.85	35.8	0.19	0.09		0.10	.004			
	Soil	2500	290	8200	290	90			13			
	Isotopes	20	20				1.3	0.4	0.3	14770	19920	13830
2 %	GEODUR	50	50									
8 %	SRPC	200		108000	320	220		320				
	Water	450	450									
	Total:	3220	810	116200	610	310	1.3	320	13.3			
No. 1A	Water content		25.2%	mg/g						kBq/g		
	w/c=		4.05	36.1	0.19	0.09	.0004	0.10	.004	4.59	6.19	4.30
	Soil	3000	264	10100	350	110			16			
2 %	GEODUR	60	60									
16 %	SRPC	480		259200	770	530		770				
	Water	710	710									
	Total:	4250	1034	269300	1130	640		770	16			
No. .	Water content		24.3%	mg/g								
	w/c=		2.15	63.4	0.27	0.15		0.18	.004			
	Soil	2500	290	8200	290	90			13			
	Isotopes	20	20				1.3	0.4	0.3	14440	19470	13520
2 %	GEODUR	50	50									
8 %	SRPC	400		216900	640	440		640				
	Water	520	520									
	Total:	3490	880	224200	930	530	1.3	640	13.3			
No. 2A	Water content		25.2%	mg/g						kBq/g		
	w/c=		2.20	64.2	0.27	0.15	.0004	0.18	.004	4.14	5.58	3.87

Table 3 continued. The product No. 4 was made only in the active version since it would not be possible to obtain hardened samples for physical characterization without the GEODUR additive.
The products 3A and 4A contains only half the activity of 1A and 2A but are similar as far as carrier concentrations is concerned.
No. 5 is similar to No. 1 but has a much lower water content.

Proportions GEODUR Cement	Recipie: g	water g	Ca	K	Na	Cs	Sr	Zn	^{134}Cs	^{85}Sr	^{65}Zn
			mg						kBq		
6 %	Soil 3000	348	9800	340	110			16			
8 %	GEODUR 180	180									
	SRPC 240		129600	380	260		380				
	Water 435	435									
	Total: 3855	963	139400	720	370		380	16			
No. 3	Water content	25.1%	mg/g								
	w/c=	4.01	36.2	0.19	0.10	.0001	0.10	.004			
	Soil 2500	275	8200	290	90			13			
	Isotopes 20	20				1.3	0.4	0.3	7310	9850	6840
6 %	GEODUR 150	50									
8 %	SRPC 200		108000	320	220		320				
	Water 405	450									
	Total: 3275	850	116200	610	310	1.3	320	13.3			
No. 3A	Water content	26.0%	mg/g						kBq/g		
	w/c=	4.25	35.1	0.19	0.09	.0004	0.10	.004	2.23	3.01	2.09
	Soil 2500	220	8400	300	90			14			
	Isotopes 20	20				1.3	0.4	0.3	7390	9960	6910
0 %	GEODUR 0										
8 %	SRPC 200		108000	320	220		320				
	Water 575	575									
	Total: 3295	805	116400	620	310		320	14.3			
No. 4A	Water content	24.4%	mg/g					kBq/g			
	w/c=	4.03	35.3	0.19	0.09	.0004	0.10	.004	2.24	3.02	2.10
Mix with decreased water content.											
	Soil 418	37	1400	50	15			2			
2 %	GEODUR 8	8									
8 %	SRPC 30		16500	50	30		50				
(of dry soil)	Water 22	22									
	Total: 478	67	17900	100	45		50	2			
No. 5	Water content	14.1%	mg/g								
	w/c=	2.20	37.4	0.21	0.09		0.10	.004			

Table 4. Composition of an ordinary concrete mortar investigated in previous studies /4/ and used as reference material here.

Concrete mortar based on sand 0.3-1 mm	Recipie:		Ca	K	Na	Cs	Sr	^{134}Cs
	g	water g	mg					kBq
Reference a	Sand 2000 Isotope SRPC 1000 Water 450	450	540000	1600	1100	4	1600	
	Total 3450	450	540000	1600	1100	4	1600	
	Water content 13.0% w/c=	0.45	156.5	0.46	0.32	mg/g 0.0012	0.46	kBq/g 4.29

It is seen that the soil products contain much more water than normal concretes and that especially the water/cement ratios are extremely high.

The homogeneity of the contamination of the active products was checked by counting 3 randomly taken 0.1 g samples of products 1A and 2A. The variation was for both products and all 3 isotopes less than 10 %, i.e. without any importance.

Based on the experience with these materials it appeared worthwhile to try to diminish the water content in the mixtures. A few inactive samples have therefore been made from a mixture (No. 5) with 8% cement and 2% GEODUR, but only with about 60 % of the water in the type 1 product. The resulting granular material could not be vibration cast but had to be ram packed into the moulds. Tentative experiments with combined use of GEODUR and a superplasticizer to obtain castable mixtures with decreased water content were not succesful.

Were relevant information is available reference will be made to an ordinary cement mortar (with w/c ratio 0.45) which has been studied previously as part of investigation of the use of concrete as barrier material for radioactive waste /4,5/, see Table 4.

3. General properties.

3.1. Compressive strength.

Inactive samples were cast in form of right cylinders with diameter 4.4 cm. After hardening ~54 days under high humidity conditions the upper ends were cut so that the height was 2 times the diameter. Only two samples of product No. 1 and one of the others were made.

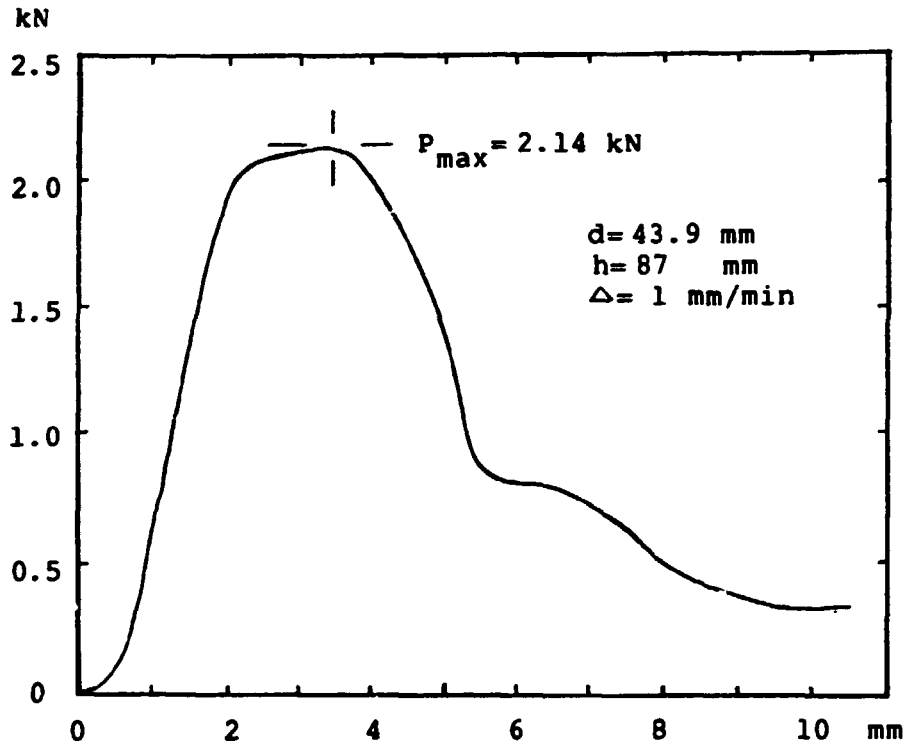


Fig. 1. Strain-stress curve for Sample No. 1b.
Product No. 1: Soil with 8% SRPC and 2% GEODUR.

The compressive strength was measured under simultaneous recording of stress-strain diagrams. The piston-traveling rate was 1 mm/minute. An example of the curves is reproduced in Fig. 1. It is fairly typical for the products that the stress is not completely relieved when the sample breaks. The material is therefore not brittle as normal concrete but is yielding more like a sample of semi-plastic material. Since random defects are not so important for the strength of unbrittle materials the results from these very few samples may be regarded as reasonably representative. The behaviour may be different with dry samples and the strength development under different storage conditions should be followed.

The compressive strengths are summarized in Table 6 together with the deformation at the point of breakage.

Table 5. Compressive strength measurements, water contents, densities and porosities of the GEODUR products.

Product type and sample	Compressive strength area = ~1500 mm²		Strain at break point h = ~88 mm	Free water: 24 h at 110°C	Water contents from table 4	Density ρ	Calculated porosities
	kNewton	MPa	mm	%	%	g/cm³	%
No. 1 a	2.29	1.51	1.6	26.5 ?	23.7	1.885	41
No. 1 b	2.14	1.41	3.4	21.5			
No. 2	6.90	4.54	1.6	19.3	24.1	1.866	42
No. 3	1.90	1.25	2.3	23.5	25.1	1.831	45
No. 5	1.80	1.19	4.6		14.1	2.05	30

It is seen that the 3 products with 8 % cement are rather similar with compressive strengths about 1.5 MPa. The sample of 16 % product (No. 2) has about 3 times higher strength. Also the hardness and the general wear resistance of this product is considerably better than for the others. Decreasing the water content gave no significant improvement of the strength (No. 5 compared with 1 and 3).

Compressive strength measurements are not available for the reference concrete mortar, but values between 30 and 50 MPa are quite normal for ordinary construction concrete.

3.2. Water contents, densities and porosities.

Table 5 does also contain a summary of the contents of free water found by drying the broken pieces from the compression strength measurements. In general there is reasonable agreement with the calculated values derived from the recipies in Table 4, especially since between 1 and 3 of the % water contents will have been taken up by the cement hydration reactions.

The product densities ρ are taken from Section 5.3. and the porosities are calculated from the formula:

$$p = 100 \cdot (2.5 - \rho)/(2.5 - 1) \quad \%$$

assuming that the mean density of the minerals is 2.5 g/cm³ and the pores are completely filled with water. The calculated porosities are very sensitive to these assumptions and the calculated values seem to be too high compared with the water contents. A significant decrease in porosity is obtained in case of product No. 5.

4. Hydraulic conductivities.

The hydraulic conductivity, K cm/sec, together with the hydraulic head, h cm H_2O, determine the apparent rate of water flow: v cm/sec through a layer thickness: x cm of the porous material under investigation. The volume of water percollating per second through an area A cm^2 is then given by:

$$w = v \cdot A = A \cdot K \cdot h/x \qquad cm^3/sec$$

The possibility of flow of water through a solidified waste material will be very important for the rate of release of micro-elements enbedded in the material, but it will also be important for the rate of degradation of the matrix material itself. A low K value is therefore desirable.

4.1. Geodur samples.

The hydraulic conductivity has been measured for the four GEODUR products (1,2,3 and 5) using 2 or 4 cm thick circular slabs (d = ~7.5 cm) cut from inactive cylinders cast and hardened in 500 ml polyethylene bottles. (The sample of product No. 5 was prepared by ramming the moist product into a 2 cm high ring.)

The samples were mounted in the cell shown in Fig. 2. The surrounding rubber rings and the conical shape of the cell chambers ensure water tightness along the sample perifery. Water was forced from a reservoir - maintained by pressurized air at an overpressure of about 50 cm Hg - through the sample. It was collected over suitable periods, weighed and in case of sample 1-2 analysed for Na and Ca.

The K values calculated according to the formula above are given as mean values in Table 7 and some are plotted in Fig 3 as function of time. Only sample 1-2 (from the standard material: No. 1, 8% SRPC + 2% GEODUR) has been run with continuous flow for an extended period. The others were kept at zero overpressure and without flow during the nights. The results are therefore not quite comparable.

The analyses of the water forced through sample 1-2 show (see also Fig. 4.) that about 65 % of the total Na and about 3.3 % of the total Ca contents in the sample were leached during the 350 hours' experiment. The total amount of water was 387 ml or 2.5 ml/g product in the sample. The Ca concentration was nearly constant = ~ 480 ppm in the out-flowing water.

The K values are seen to decrease slightly with time (except sample 5-1 which may have developed a slight defect). Leaching due to the water flow through the sample is therefore not sufficient to compensate for another mechanism resulting in some closure of the pore structure. Much more pronounced decreases in K values with time have been seen in other experiments, especially for some types of low w/c ratio ordinary concrete /6/.

The hydraulic conductivity of the GEODUR material No. 1 is nearly the same as for the reference cement mortar with w/c = 0.45. The much higher porosity of the GEODUR samples does therefore not result in a corresponding increase in water permeability. The reason for this is no doubt the clay content in the soil.

Table 6. Hydraulic conductivities obtained for samples of GEODUR-solidified soil. The reported values are mean values over the periods with water flow. Only periods with water flow are included in the time column. The measurements are also used to identify samples of sufficient quality for use in the diffusivity experiments (see Section 6)

Product No	Cement %	Water %	Sample No	Thickness cm	time h	flow ml/h	K cm/sec
1	8	23.7	1-1 1-2 1-3	1.90 1.95 2.05	170 348 23	1.06 1.15 1.40	$2.29\ 10^{-8}$ $1.95\ 10^{-8}$ $2.75\ 10^{-8}$
2	16	24.1	2-1 2-2 2-3 2-4	2.0 2.1 4.3 2.01	defect defect 27 31	high high 0.10 0.35	 $0.42\ 10^{-8}$ $0.78\ 10^{-8}$
3	8	25.1	3-2	2.05	16	1.03	$2.02\ 10^{-8}$
5	8	14.1	5-1 5-2	2.27 2.00	25 6	0.23 0.34	$0.59\ 10^{-8}$ $0.63\ 10^{-8}$

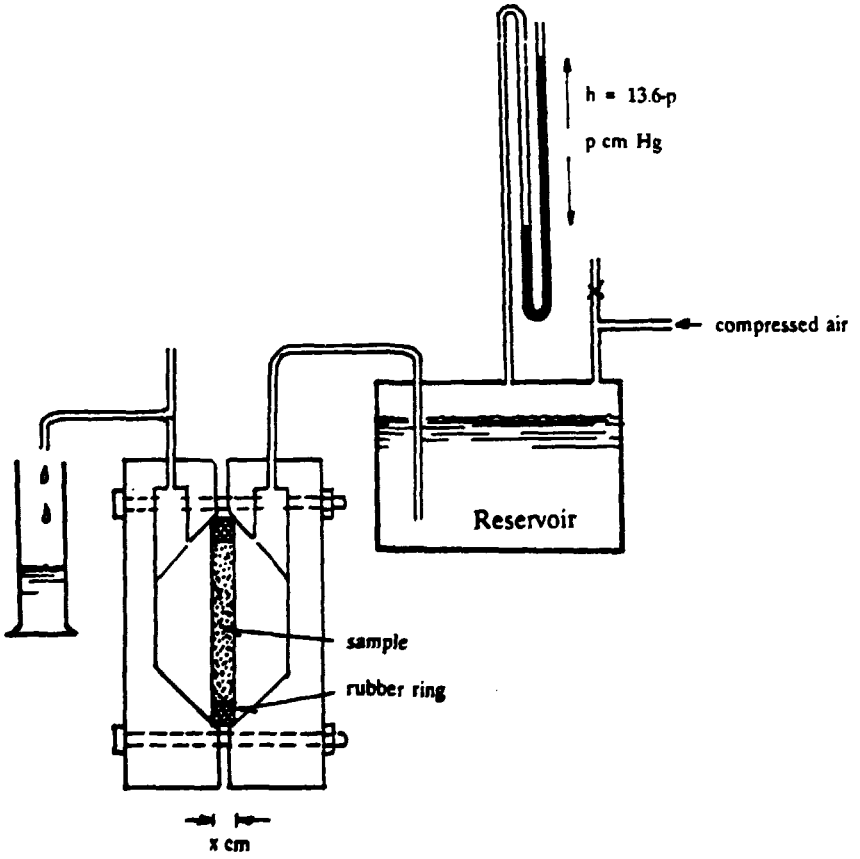


Fig. 2. Experimental set-up for determination of hydraulic conductivity in concrete disks. The system can also be used to study leaching with flow through the pore system although some diffusive leaching will occur simultaneously.

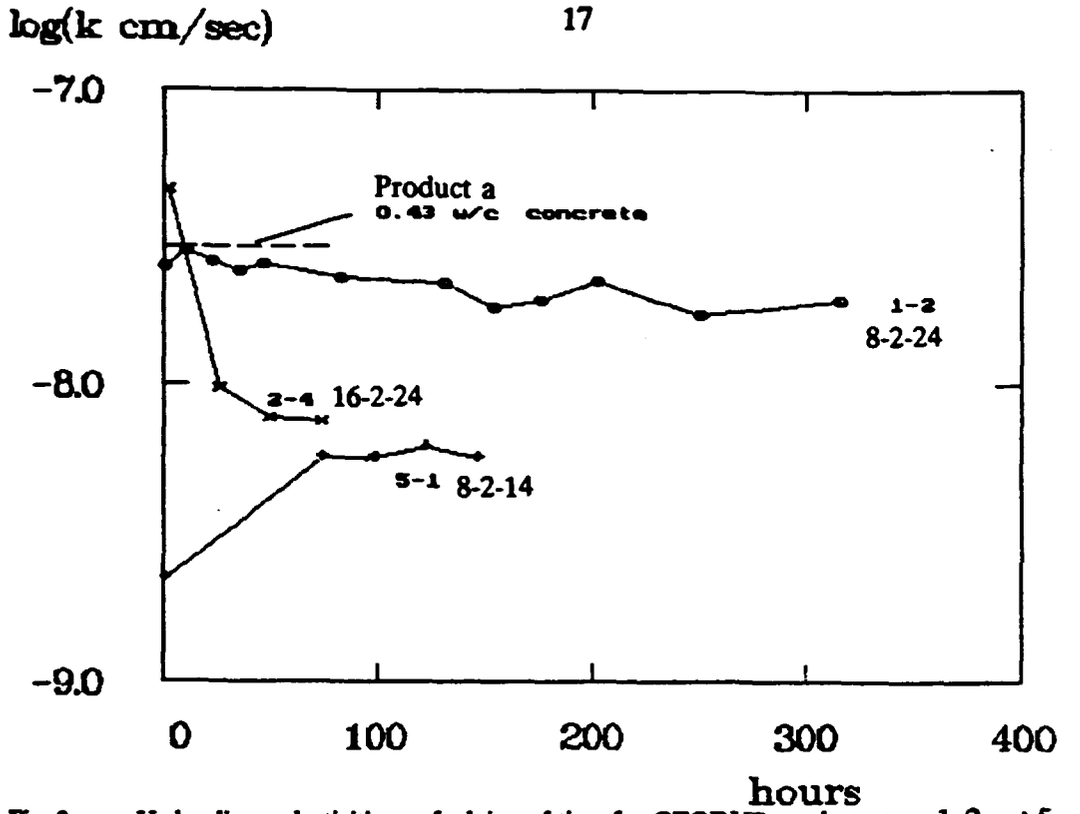


Fig. 3. Hydraulic conductivities as funktion of time for GEODUR products, type 1, 2 and 5. The conductivity for the reference concrete mortar a is also indicated.

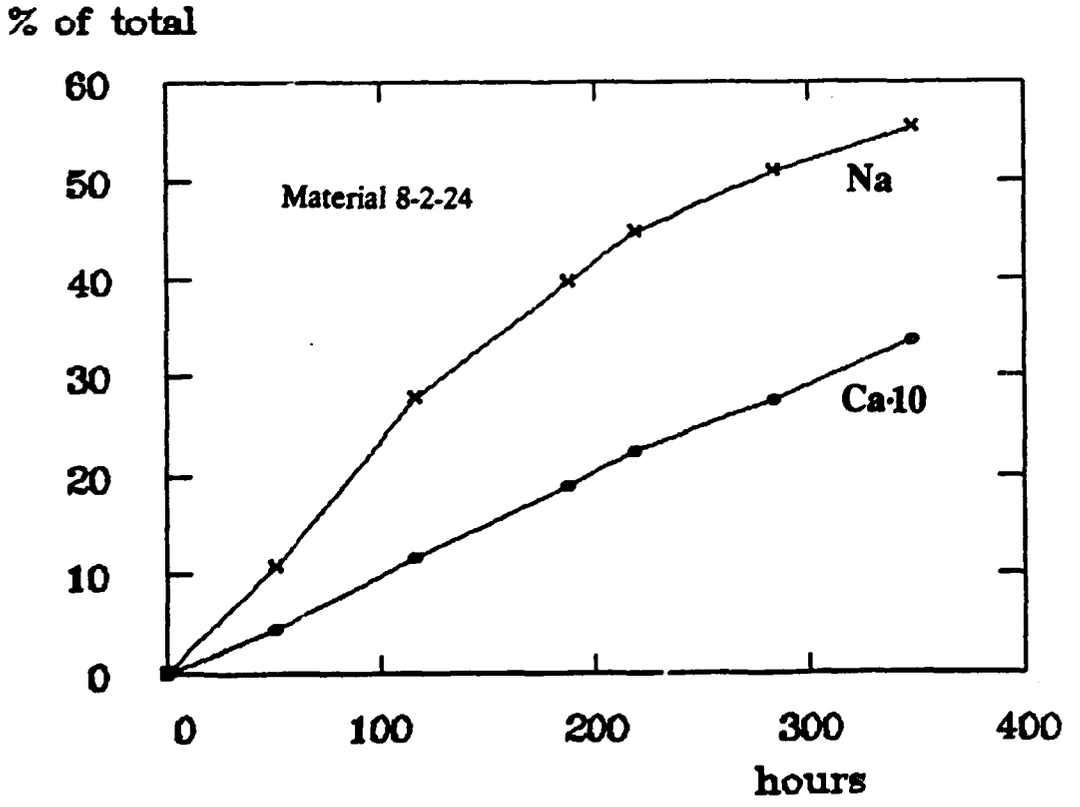


Fig. 4. Sodium and calcium leached from the sample of GEODUR product, type 1 as fractions of the amounts originally present in the disk.

4.2. Soil.

For comparative purposes the permeability of the soil as such without any cement admixture was also measured. It was done simply by packing soil with known water content in a ~4 cm layer on top of a supported filter paper at the bottom of a column. It was then left standing with ~50 cm water covering the soil layer and the percolating water was collected occationally during some weeks.

The mean hydraulic conductivity was $8.4 \cdot 10^{-8}$ cm/sec at 24.6 % water in the soil and $4.4 \cdot 10^{-8}$ cm/sec at 18.6 % water. The water contents were controlled after the experiment and had increased to 25.6 % in the upper few mm accompanied by a few mm swelling. Comparison with the K values for the GEODUR products with 24 % water (see Table 7.) indicates that the treatment results in an improvement of a factor 4 to 10 in the permeability relative to unmodified soil with similar water content.

5. Leaching experiments.

The evaluation of the long-term quality of cement-conditioned waste products requires knowledge about leach rates for the pollutants (normally a very minor component) as well as the rate of release of the major components, primarily calcium and hydroxyl ions. In the long run extensive leaching may result in pH decreases and even loss of physical strength. Reaction with CO_2 from the environment is another mechanism which may result in pH decreases in the product. The low cement content and the porous structure of GEODUR-cement-solidified soil is likely to make the product more sensitive to changes of this type than in case of ordinary concrete, but - as seen from the following - the effects may not necessarily be negative.

Various experiments have been made to elucidate these phenomena. However, so far the results can only be regarded as tentative.

5.1. Active samples cast in polyethylene flasks.

As mentioned previously active samples of the 4 products specified in Table 3 have been cast in form of ~4 cm thick layers in the bottom of 500 ml polyethylene flasks. The samples were hardened in the flasks with closed caps for 33 days. Four samples of each product was made. One of each was exposed at 20°C to either deionized CO_2-free water (caps closed), deionized water with CO_2 access (open to the atmosphere), 3 % NaCl solution (partly simulating sea water, caps closed) and, 3 % NaCl solution with CO_2 access (open to the atmosphere). The matrix of experiments is shown in Fig. 5.

In leaching experiments of this type the wall of the soft polyethylene flasks should normally have been sqeezed against the top of the cylindrical surface of the hardened sample by an external rubber ring surrounded by a steel clamp. This is done to avoid leaching via gabs between sample and container which may arise due to contraction of the sample during hardening. However, due to the lack of strength of the control material No. 4 it was prefered to omit the feature for all the systems.

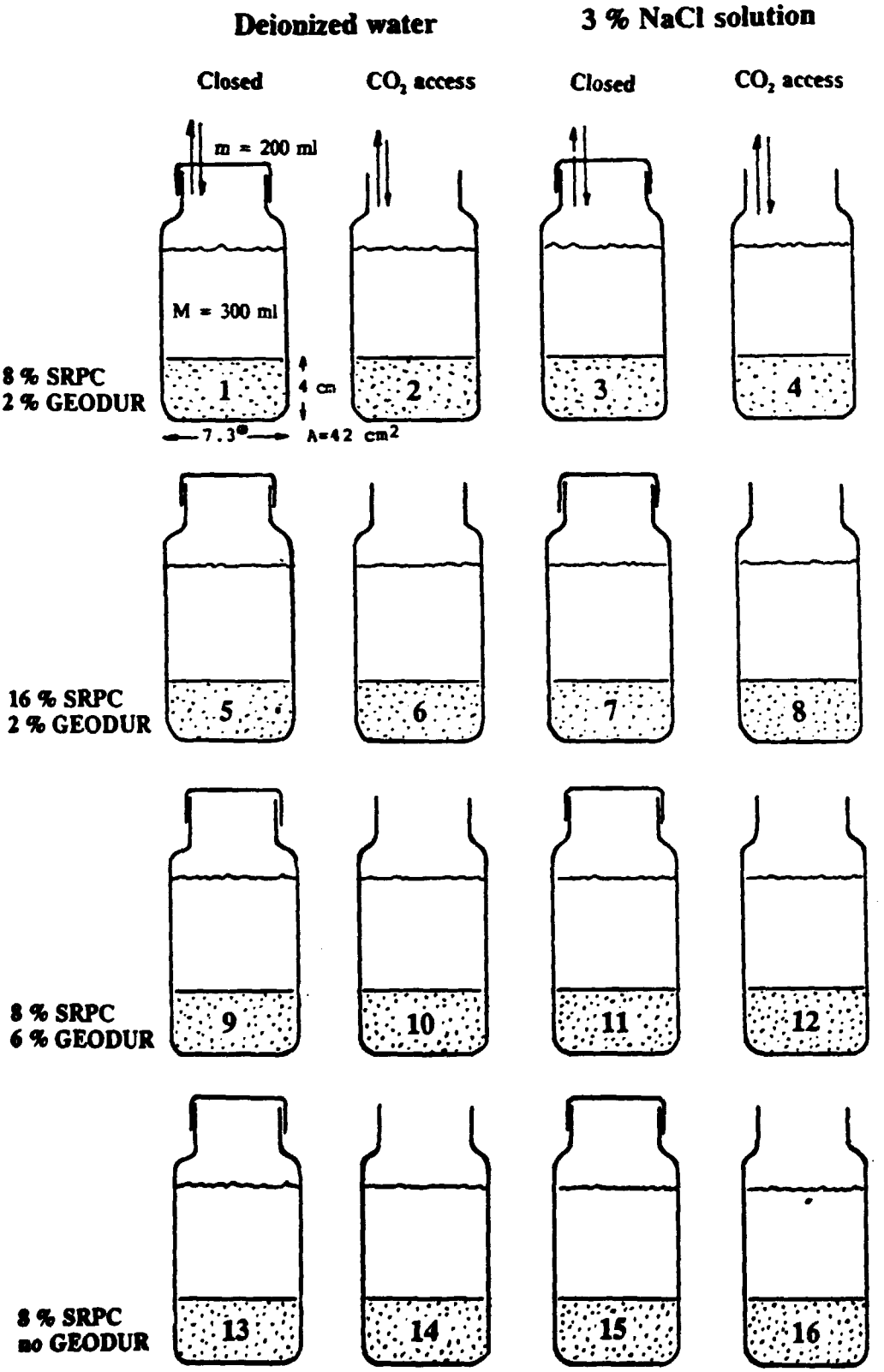


Fig. 5. Systems used in measurement of diffusive leaching from thick samples of the three GEODUR products and the control without the additive.

The initial volume of leachant was M=300 ml. A sample m=200 ml of this was removed and replaced with fresh solution after leaching periods of 3, 5, 6, 7, 14, 21, 21, and 21 days, respectively. pH was measured in the solution samples which were then analysed for ^{134}Cs, ^{85}Sr and ^{65}Zn by γ-spectroscopy. Ca has been determined by AAS but only for the closed systems since some floating $CaCO_3$ precipitates would have given rather uncertain results for the open systems.

The Cs and Sr results are presented in Figs. 6a-h and 7a-h in form of leach curves, i.e. the equivalent leached thickness L plotted against the square root of time. The ordinate corresponds to the thickness of the surface layer which orignally contained the accumulative amount of activity removed with the water samples. It is (with suitable corrections for decay) given by the expression:

$$L_n = (M \cdot c_n + \sum_{1}^{n-1} m \cdot c_n) / (A \cdot C_o) \qquad cm$$

where c_n is the concentration in the n'th water sample, A is exposed sample surface area (42.0 cm^2), and C_o the original concentration in the product e.g. in Bq/cm^3.

In principle (see comment above) it is only the upper surface of the sample which is exposed to the water and the leaching can therefore be regarded as taking place under one-dimensional conditions. If the rate of release is controlled by diffusion the formula

$$L = 2\sqrt{(D \cdot t/\pi)}$$

is valid as long as L is less than about half the total thickness of the sample (~4 cm) and the concentrations in the solution above the sample is low compared with the concentrations inside the sample. If L plotted against $\sqrt{t}$ results in a straight line a value for the diffusion coefficient D can be obtained from the slope of the curves. This has been done for the curves in Figs. 6a-h, 7a-h and 8a-d. The results are given in Table 8.

The D values may be used to calculate releases from the material in other geometries and is a measure for the quality of the product: the lower the value the better the product.

The leach rate will decrease with time and thickness of the leached layer. The value e.g. at 100 days can be obtained from the formula:

$$S_{100} = \sqrt{(D \cdot 24 \cdot 3600/\pi \cdot 100)} = 16.6\sqrt{D} \qquad cm/day$$

5.1.1. Leaching of Cs.

Comparing the Cs-curves in Figs. 6a-h and 7a-h and the D-values for ^{134}Cs in Table 8 the following conclusion may be drawn:

- The leaching of Cs is low under all circumstances but highest in the 3% NaCl solution. The leach rates at 100 days are of the order $2 \cdot 10^{-5}$ to max. 10^{-3} cm/day and the thickness of the equivalent leached layer between 0.1 and 2 mm.
- The leach rates for Cs is considerably lower from these products than from ordinary concrete or cemented waste products without soil.

- The leaching appears to be higher from the product with 16% SRPC compared with the ones with 8% SRPC.
- CO_2 access results in a slight improvement mainly in case of the systems exposed to deionized water.
- No significant improvement appears to be obtained by the use of the GEODUR additive, i.e. in this fixed geometry it is not so important whether the material solidifies into a solid block or simply is present as a soft layer on the bottom of the flask.
- Contaminated soil without cement was not included among the systems, but the experiment has been done later /8/. It was found that the release rate for this soil with high clay content was considerably less than for the cementitious materials.

Most of these features can probably be explained as an effect of ion-exchange competition. It is well known that Cs (at the very low concentrations present here) is retained quite efficently by soil minerals. However, in NaCl solution and in Ca^{++} containing pore water in a cement product it may still tend to be released by the other cations.

5.1.2. Leaching of Sr.

The Sr-curves in Figs. 6a-h and 7a-h and the corresponding D values in Table 8 indicate a quite different behaviour for this element.

- The leaching of Sr is rather high in all the closed systems, somewhat higher in the 3% NaCl solution than in deionized water. The leach rates at 100 days are between 6 and $4 \cdot 10^{-3}$ cm/day and the thickness of the equivalent leached layer from 7 to 11 mm.
- The leach rates for Sr is considerably higher than for ordinary concrete or cemented waste (although the literature values may be influenced by CO_2).
- There is not much difference in behaviour of the four types of materials when leached in water or NaCl solution without contact to the atmosphere. The leach curves are nearly linear.
- This is not the case for the systems with CO_2 access where a marked decrease in release rates appears after some time. The D values given in Table 8 corresponds to the slope of this later part of the curves. The leach rates at 100 days are reduced about a factor 10. The reason may be precipitation of Sr as carbonate within the pore structure of the product. However, its should be noticed that the curves for the three products with 8% cement are starting to climb again at the end of the period where the pH are reaching values about 9.5 and solubilization as bicarbonate begins to be a possibility, see Fig. 7a,c and d. CO_2 access may therefore only be a temporary advantage. The buffering capacity of the product with 16% cement is of course somewhat higher.
- Again no significant improvement is obtained by the use of the GEODUR additive with this sample configuration.
- Sr leaching from the soil without cement was studied in later experiments /8/. The diffusive release is intermediate between the behaviour of the cementitious materials with and without CO_2 access.

For the systems without CO_2 the Sr release can probably be explained quite well by simple ion-exchange theory taking into account that the strontium ion is divalent. The relatively high amount of strontium carrier introduced with the cement (typical content ~0.1%) is important for the ion exchange behaviour as well as the precipitation reactions when CO_2 is present.

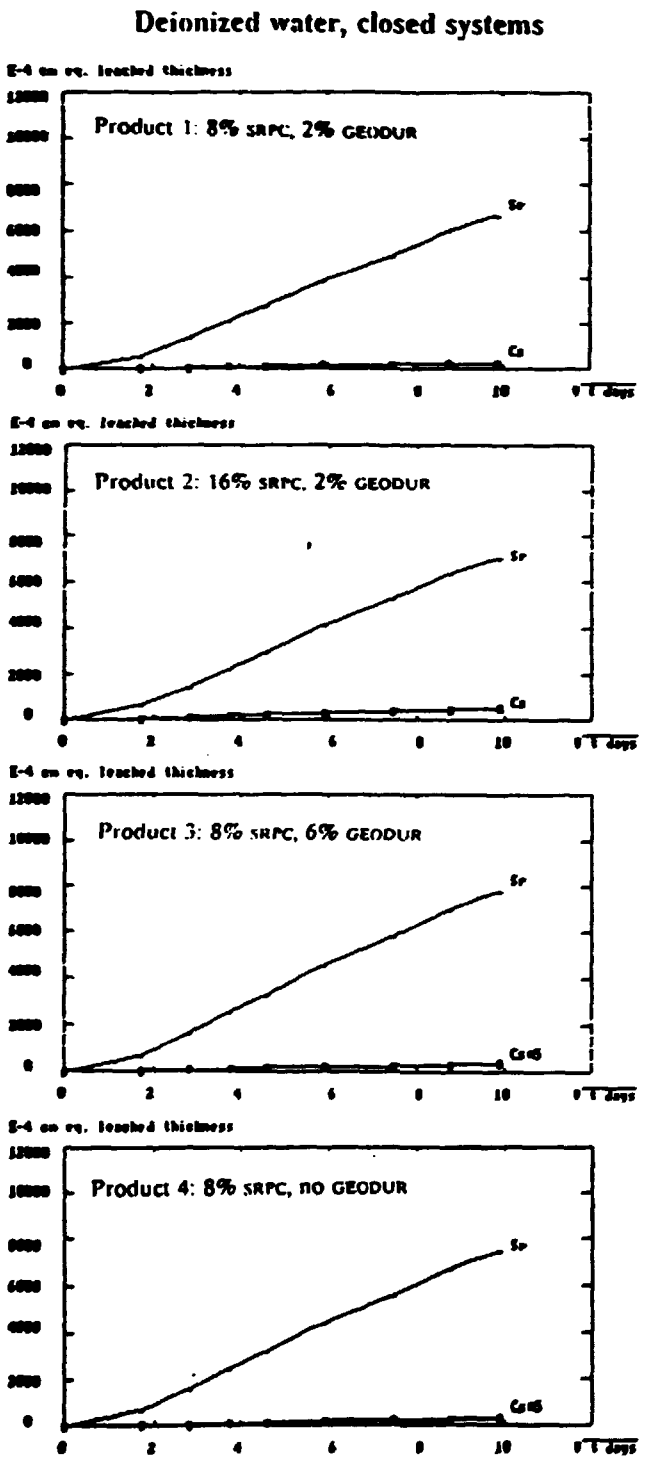


Fig. 6 a,b,c,d

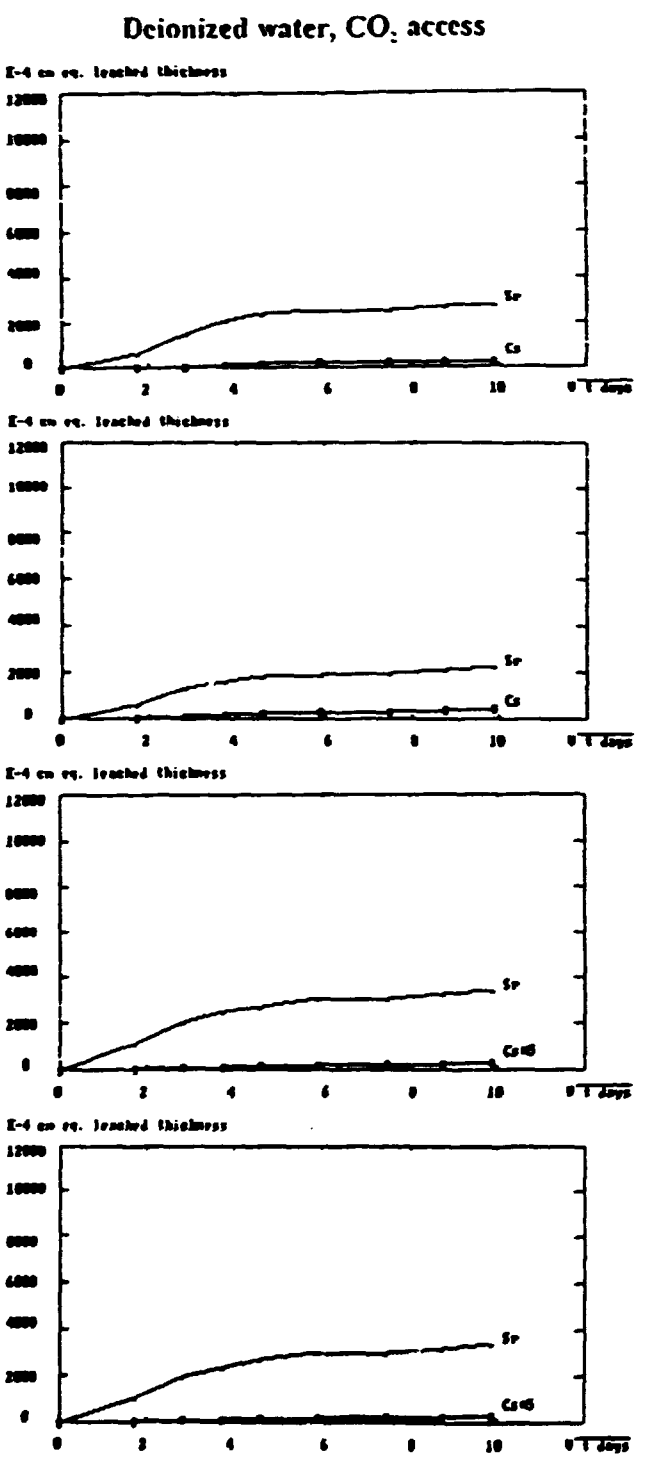


Fig. 6 e,f,g,h

Leaching in deionized water of ^{134}Cs and ^{85}Sr from samples of the three soil/cement products prepared with the GEODUR additive and the control without the additive.

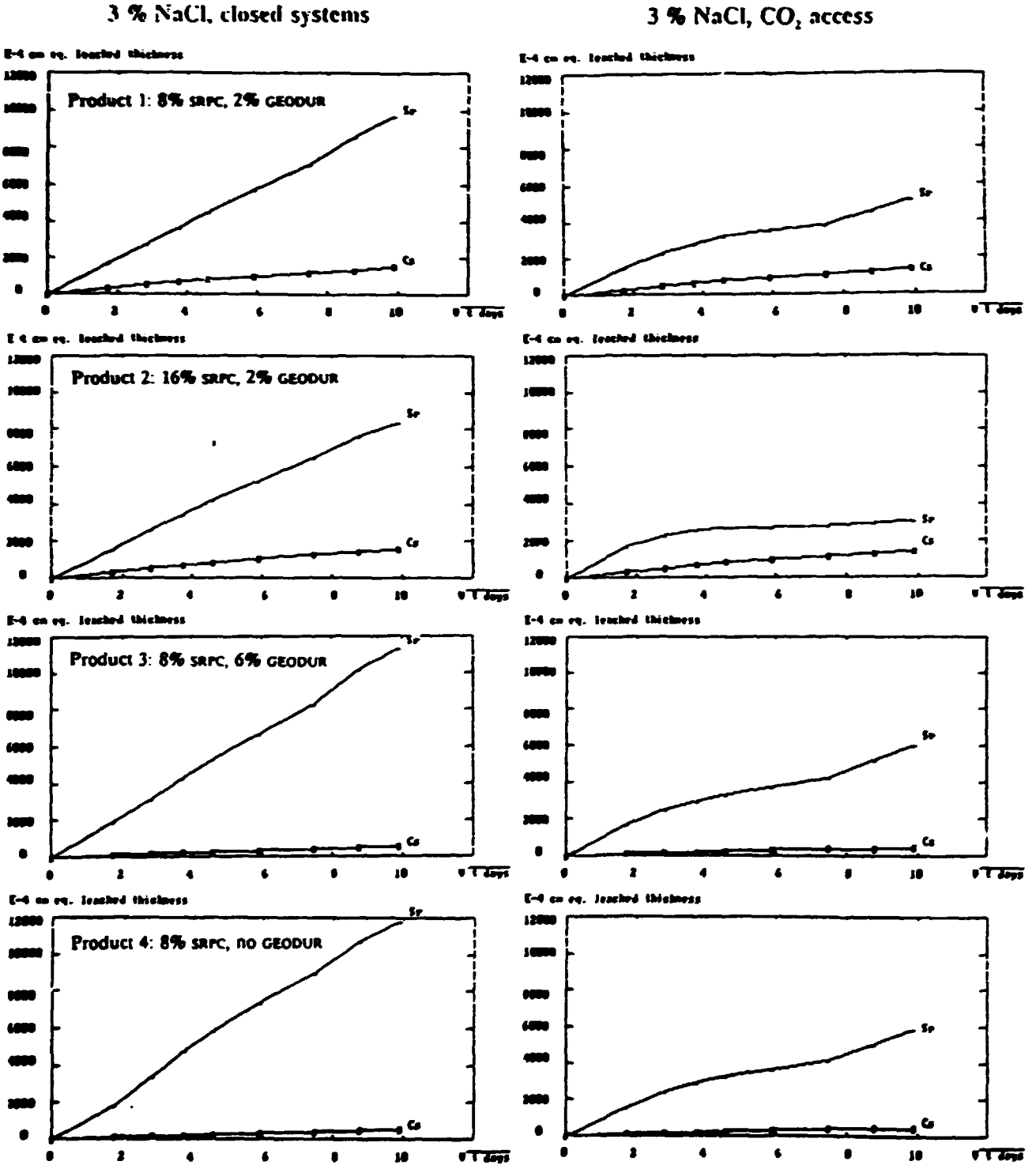


Fig. 7 a,b,c,d

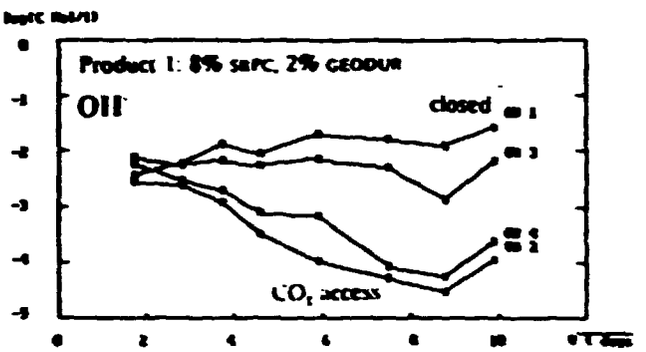
Fig. 7 e,f,g,h

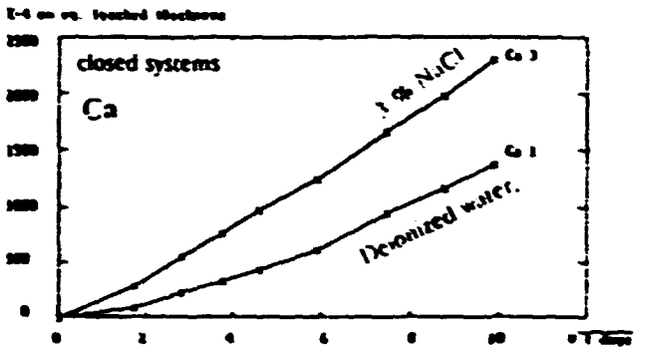
Leaching in 3 % NaCl solution of ^{134}Cs and ^{85}Sr from samples of the three soil/cement products prepared with the GEODUR additive and the control without the additive.

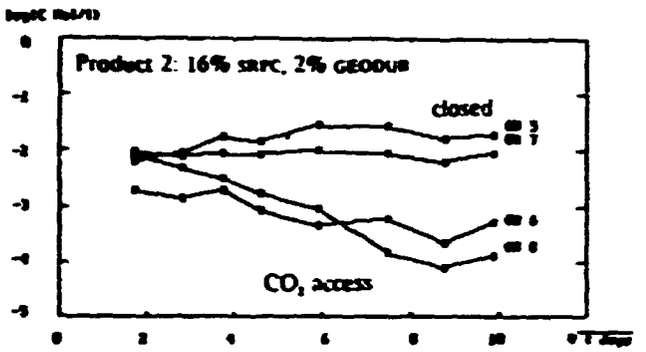
Table 7. Effective diffusion coefficients obtained from leaching of ^{134}Cs, ^{85}Sr and Ca under 4 different conditions from samples of the three products prepared with GEODUR and the control of soil + cement but without the additive. For comparison values for the soil without cement and for a typical construction concrete are also given.

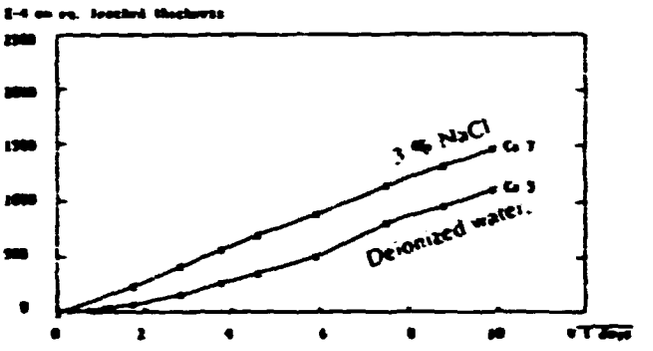
		D_e unit: 10^{-9} cm^2/sec			
		Deionized water		3 % NaCl solution	
		Closed	CO_2 access	Closed	CO_2 access
1					
	^{134}Cs	0.098	0.025	1.92	1.21
8 % SRPC	^{85}Sr	52	0.35	86	~11.4
2 % GEODUR	Ca	2.34	-	5.5	-
2					
	^{134}Cs	0.35	0.20	2.1	1.26
16 % SRPC	^{85}Sr	58	0.52	61	0.56
2 % GEODUR	Ca	1.57	-	2.1	-
3					
	^{134}Cs	0.0061	0.0026	0.23	0.20
8 % SRPC	^{85}Sr	71	1.46	121	~22
6 % GEODUR	Ca	3.0	-	5.5	-
4					
	^{134}Cs	0.0051	0.0024	0.24	0.19
8 % SRPC	^{85}Sr	64	1.31	133	~19.3
0 %	Ca	2.7	-	5.7	-
Soil without cement (15% water) from ref /8/.					
0 %	^{134}Cs	0.00002		2.0	
0 %	^{85}Sr	1.9		56	
Cement mortar in typical construction concrete, from ref /7/.					
a cement mortar w/c=0.45	^{134}Cs	51			
	^{85}Sr	0.001	in somewhat different materials and probably influenced by CO_2		
	Ca	0.04			

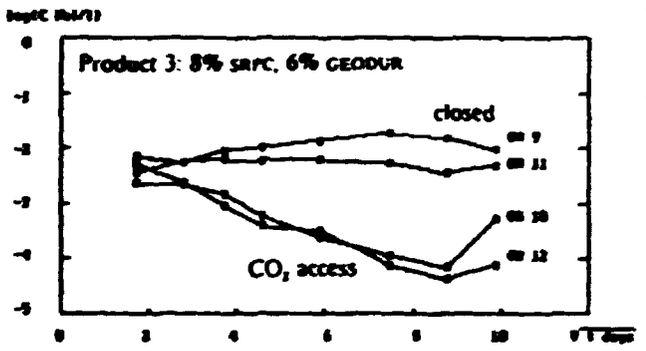
~ indicates that the release may be due to solubilization with HCO_3^- ions.

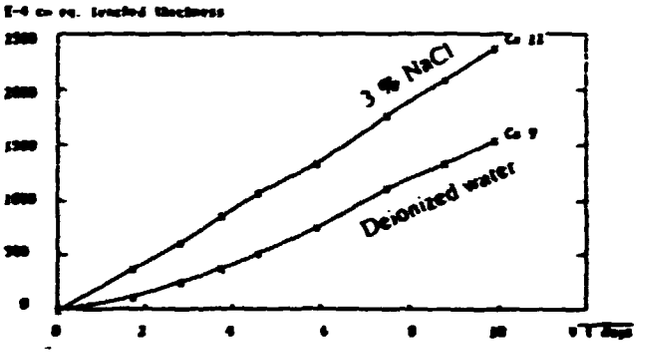


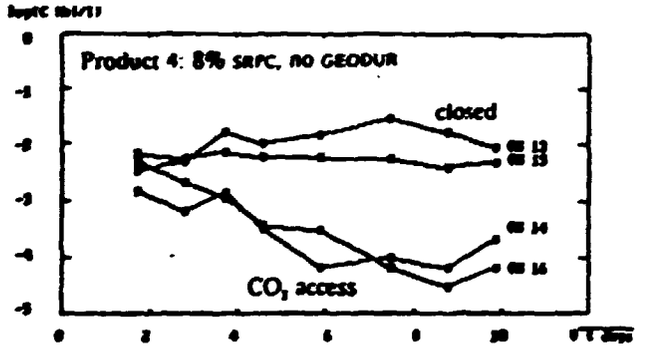












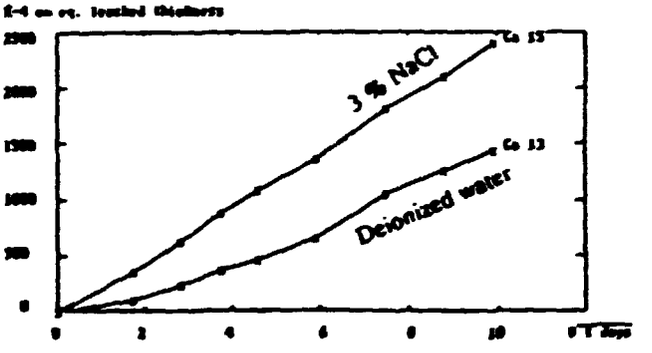


Fig. 8 a,b,c,d

The pH development given as OH^- concentrations for all 16 systems.
(The system numbers are shown on Fig. 5)

Fig. 9 a,b,c,d

Calcium leach curves for the 8 closed systems without CO_2 access.

5.1.3. Leaching of Ca.

The Ca leach curves for the closed systems are shown in Figs. 8a,b,c,d. The behaviour of the 3 materials with 8% cement is nearly identical and also in agreement with the 16% product since the Ca concentration in this product is about a factor 2 higher. Leaching is highest in NaCl solution, maybe reflecting a higher solubility of Ca components in this medium. However, the linear dependence on $\sqrt{t}$ indicates that diffusion and not simply solubility limitations is the regulating release mechanism also for Ca under these circumstances. The equivalent leached thickness is ~2 mm after 100 days. However, the more easily dissolvable $Ca(OH)_2$ is probably extracted to a considerably larger depth (maybe approaching the 5 to 10 mm typical for Sr) leaving a diffusion barrier of more slowly degradable hydrated calcium silicates at the surface.

5.1.4. Leaching of Zn.

As mentioned above the solution samples were also analyzed for ^{65}Zn by γ-spectroscopy. However, the countings were in no cases significant, i.e. the concentration was always below ~1 Bq in 50 ml (~0.02 ppb Zn) corresponding to an equivalent leached layer of maximum 0.001 mm after 100 days. The leach rate is therefore below 10^{-6} cm/day, i.e. considerably better than the best results obtained for Cs.

This may well be characteristic for the release of heavy metals from the products but should of course be verified by experiments better designed for the purpose. The release rates may depend rather much on the concentration of the heavy metal in the soil.

5.2. Broken pieces.

A different approach to the study of leaching behaviour of cemented products is to measure the releases after fracturing or granualtion of a sample of the material. In this case the geometry-dependent diffusion-controlled leach rates are (partly) suppressed and the results are more directly related to the chemistry of the systems.

5.2.1. Hardened without CO_2 access.

Small pieces with typical dimensions 0.5 cm were made by breaking partly hardened plates of the 3 GEODUR-containing products. Similar pieces albeit very friable could also be obtained from the soil+8% SRPC but without the additive. After complete hardening with at least partial protection against carbonation about 20 g of each product was immersed in M=200 ml water in polyethylene bottles. The leaching was then followed by sampling and replacement of m=150 ml using the same time scedule as in the experiment above. Deionized water was employed in systems with and without CO_2 access. The systems are shown in Fig. 10.

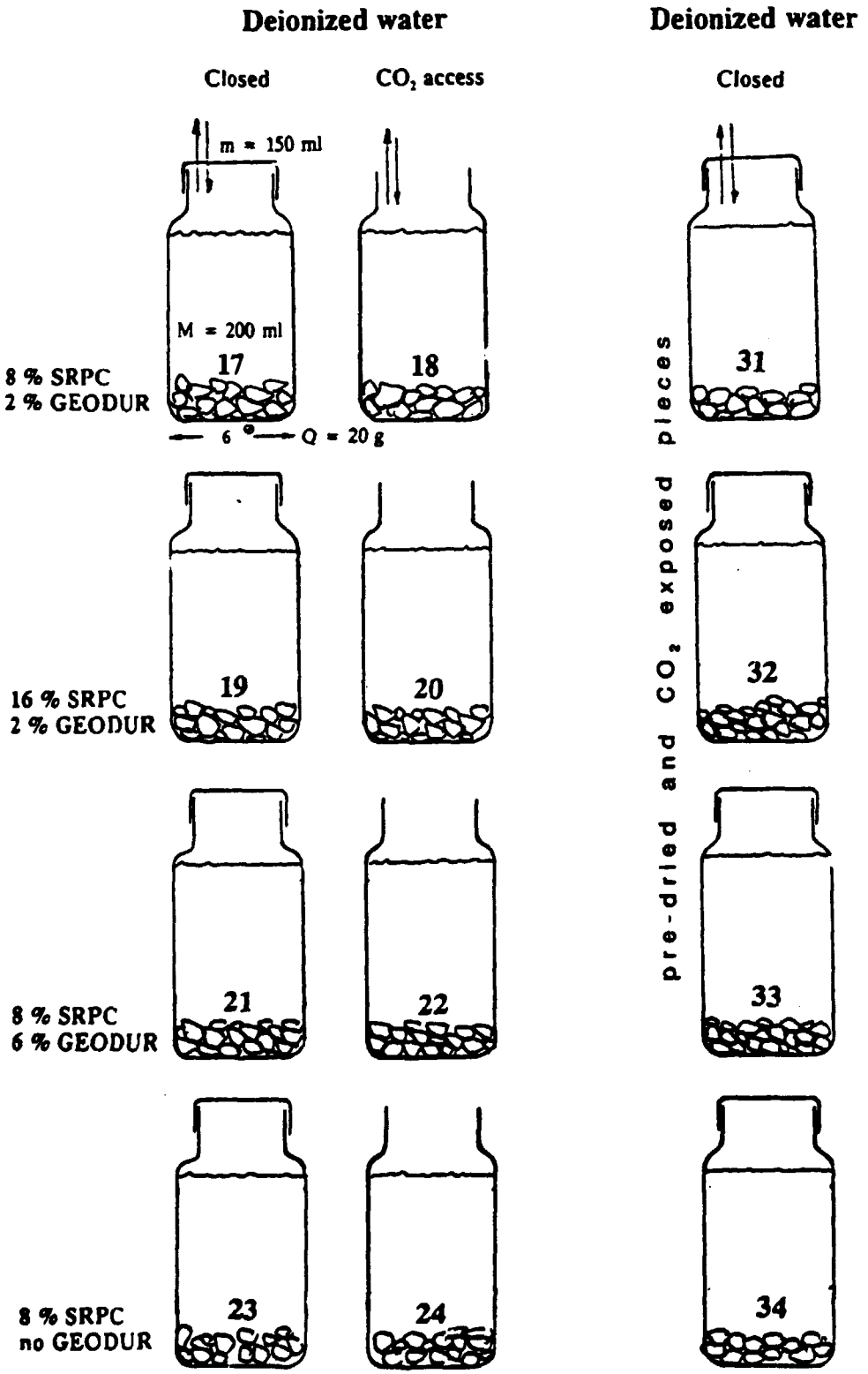


Fig. 10. Systems used in measurement of leaching from broken pieces of the three GEODUR products and the control without the additive. The systems to the right was employed in an additional experiment with pieces pre-dried under CO_2 exposure.

With small pieces af irregular shape the concept of an equivalent leached thickness is not applicable and the results are therefore presented as leached fractions, i.e. the accumulative amount of activity found in the water divided by the original amount present in Q g of material with density ρ g/cm^3:

$$F_n = \Sigma a/a_o = (M \cdot c_n + \sum_{1}^{n-1} m \cdot c_n) / (Q \cdot C_o/\rho)$$

The leached fractions are plotted against the volume of water (in ml/g product) which has contacted the pieces, see Figs. 11-14.

The treatment is even more severe than in the previously described experiment. During the 120 days exposure the pieces were contacted by about 70 ml water per g material. The typical dimension of these rather porous pieces is only about 5 mm and easily leached materials is therefore expected to be removed nearly completely by the treatment. The release of less easily leached materials tends to be regulated by ion-exchange equilibria or by solubility limitations although true equilibrium may not be reached due to e.g. lack of stirring during the leaching periods.

The tendency as far as cesium is concerned is the same as for the solid blocks: compare Figs. 11a and 12a with e.g. Table 8. Cs is leached most readily from the product with 16% SRPC. The 8% SRPC+2% GEODUR has an intermediate position while the releases are lowest for the products with 8% SRPC+6% or no GEODUR. The reason for this apparently similar effect of absence or an overdose of the additive is not clear. The increased release from the 16% SRPC product can be ascribed to higher concentrations of e.g. Ca^{2+} ions competing with Cs^+ about the ion-exchange sites on the soil. About 6 % of the cesium has been leached, but this is still much better than for an ordinary concrete where more than 90 % would have been extracted under similar circumstances. The curves for the systems with and without CO_2 access are nearly identical.

The opposite is the case for strontium. In the closed systems about 70-80 % are leached while the fraction is about 50 % in the systems open to the atmosphere. More than 4/5 of the leaching takes place during the two relatively short initial leaching periods (3 and 4 days) where the influence of indiffusing carbon dioxide must have been slight.

No or practically no ^{65}Zn release could be measured.

Calcium analyses are only available for the closed systems. However, it should be noticed (Fig. 13a) that the leached frations are nearly the same for the product with 16 and the others with only 8 % cement. The reason is probably that twice as much $Ca(OH)_2$ is formed in the 16 % product and the total amounts of calcium hydroxide in all cases are leached rapidly.

The Ca-concentrations are fairly constant so that the leached fractions are increasing linearily with the volume of water (Fig. 13a,b). In this case more than 30 % of the total Ca was leached i.e. considerably more than the maximum amount of $Ca(OH)_2$ generated by hydration of the cement minerals. Some degradation of hydrated calcium silicates must therefore have taken place.

Broken pieces, closed systems.

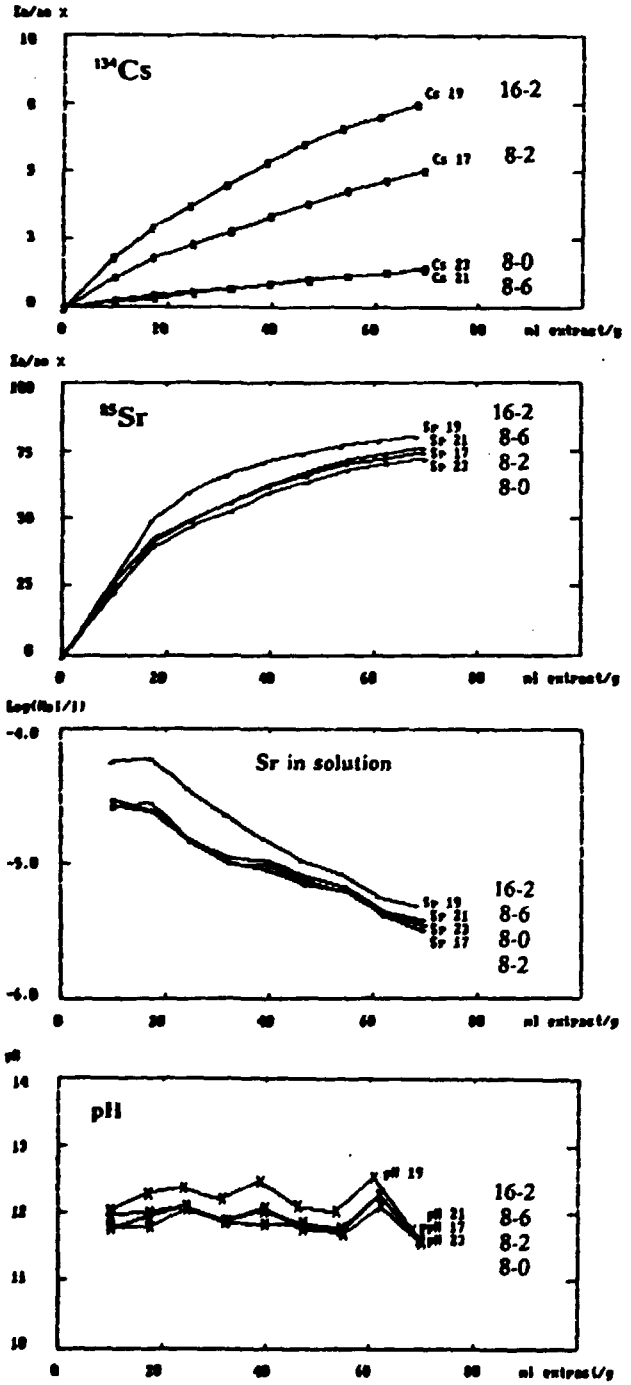


Fig. 11 a,b,c,d.

Broken pieces, open systems with CO_2 access.

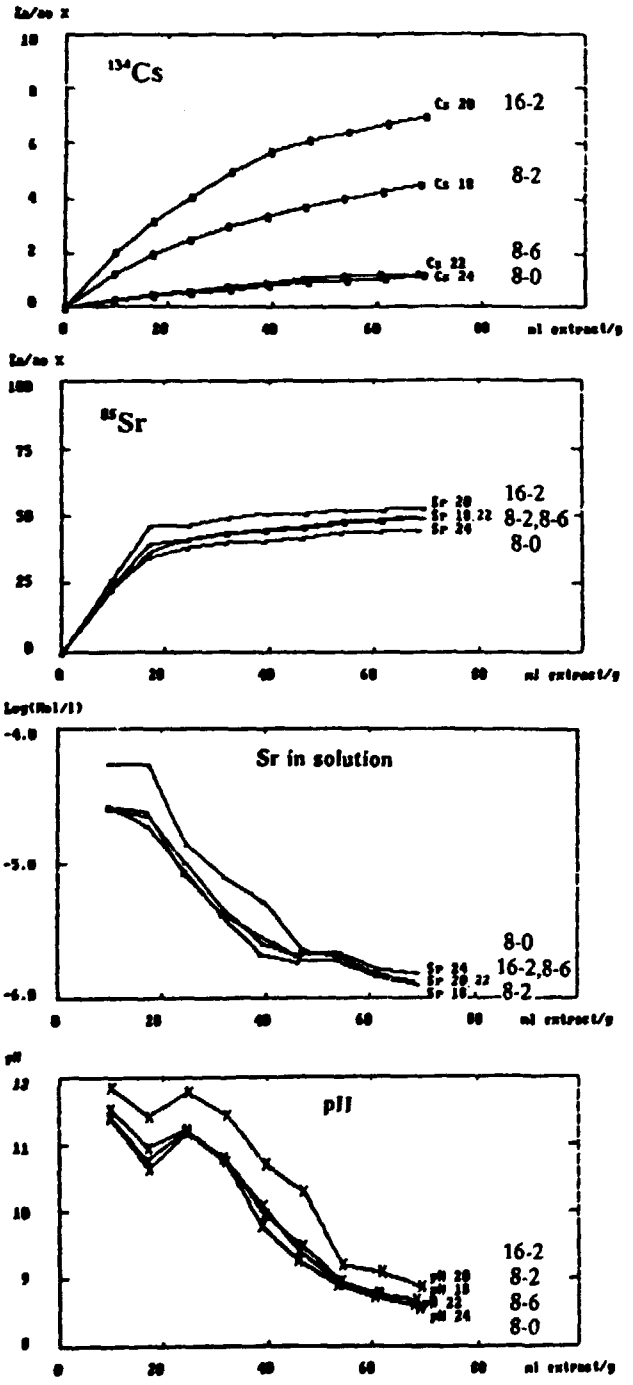


Fig. 12 a,b,c,d.

^{134}Cs an ^{85}Sr leach curves, Sr concentration in the solutions and pH development for the systems with broken pieces in deionized water without or with CO_2 access.
(The system numbers are given in Fig. 10, the numbers 16-2, etc. refers to the approximate contents of cement and GEODUR additive in the 4 types of materials).

The pH is much dependent on whether the systems are open or closed. It decreases slowly but remains near 12 in the closed systems. In the open systems it has dropped to below 9 after 120 days and 9 samplings. There is no indication of negative effects on Sr release due to the decreased pH and the possibility of increased HCO_3^- concentration in the solution as was the case with the systems described in Section 5.1.

5.2.2. Dried and carbonated during hardening.

To investigate whether the beneficial influence of carbonation on Sr release could be improved an additional experiment was made where broken pieces of the four products were left exposed to the atmosphere for about 50 days. During this period the samples dried out to equilibrium with the humidity in the atmosphere and at least partial carbonation of $Ca(OH)_2$ took place. The pieces were then immersed in water in closed bottles.

The Cs and Sr leach curves are shown in Figs. 14a,b. The experiment has not been run for as long time as the others but it appears that the released fraction of Sr is reduced about a factor 3 compared with the other closed systems. Ca leaching is reduced about a factor 2, compare Fig. 13a and 13c. The pH is increasing with time and with the partial replacements of solution taking place at each sampling (Fig. 14d). This may indicate some slow degradation of hydrated calcium silicate from the cement. The increase would of course not have occured in systems open to the atmosphere.

In closed systems with $CaCO_3$ as well as $Ca(OH)_2$ present as solid phases the equilibrium composition of the solution is fixed: From the solubility products and the electro neutrality requirement it is calculated that the pH is ~12.4, the carbon dioxide pressure pCO_2 ~$2 \cdot 10^{-13}$ atm and the corresponding CO_3^{--} concentation ~$7 \cdot 10^{-7}$ mol/l. The Ca^{++} and Sr^{++} concentrations are then 0.012 an 0.002 mol/l, respectively.

The calculated pH, the Ca- and especially the Sr-concentrations are seen to be higher than found in the experiment with the carbonated broken pieces (Figs. 14d, 13d and 14c), although there is a tendency to better agreement for the 16-2 product. The explanation is probably that no or practically no free calcium hydroxide from hydration of the cement is remaining in the carbondioxide reacted product so that the solution pH and the calcium concentrations are determined by the more complicated degradation of the hydrate calcium silicate gel. The influence on the Sr concentration may be indirect through increased CO_3^{--} concentrations but could also be due to silicates. The measured concentrations are nearly constant in time. This is reflected in the straight line relationships between leached Ca and Sr and the amount of water which has contacted the samples.

It is interesting to note that the drying and carbonation treatment has a profound effect on the Cs releases. Not only are they reduced a factor 3 or more, but the order of the quality of the materials is changed. The 16 % SRPC product is no longer the one with highest release but is now considerably better then the others: the factor of improvement is about 50 (compare Figs. 12a and 14a). The mechanism may be associ-ated with the drying of the clay particles and collapsing of the molecular structure.

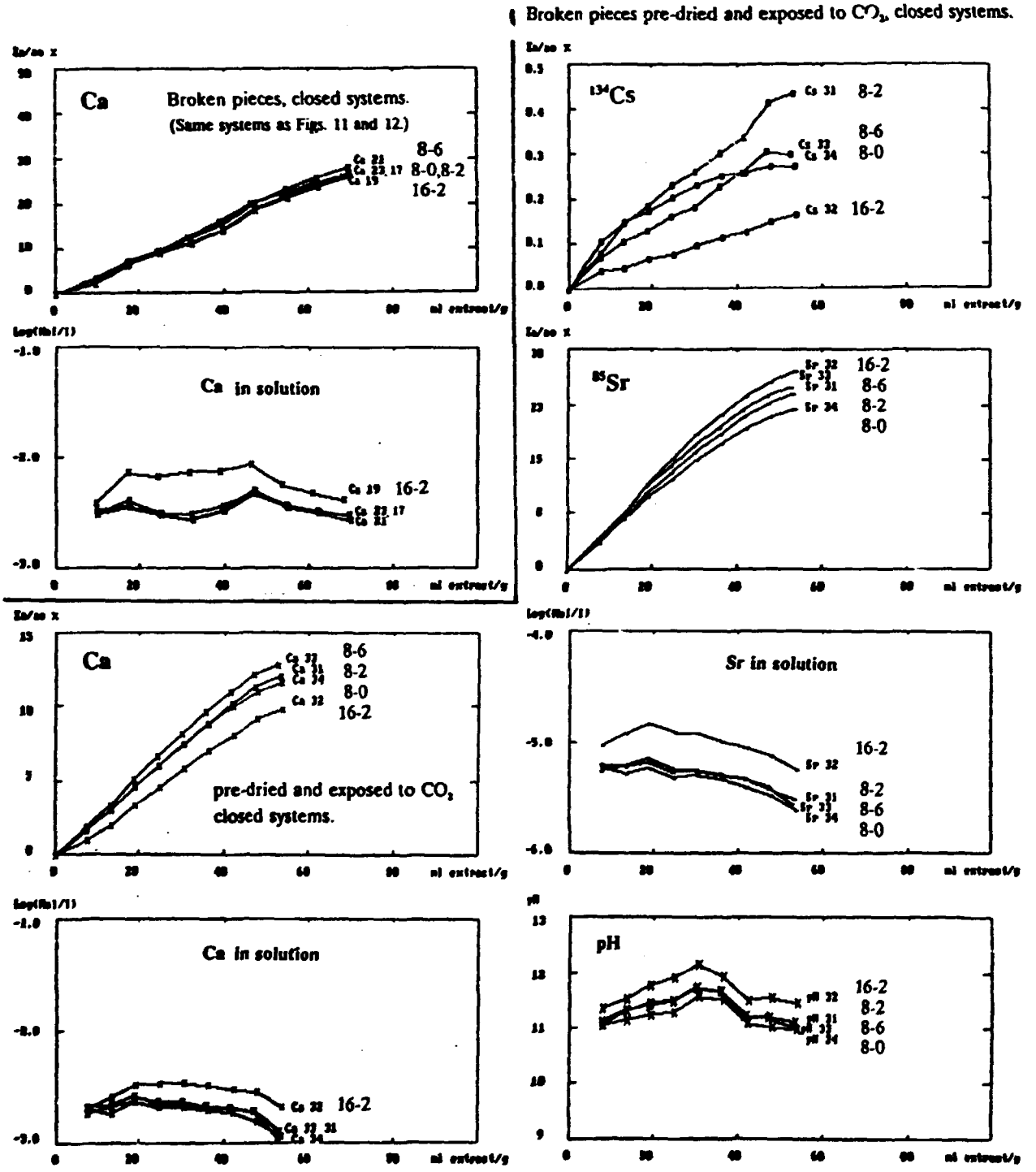


Fig. 13 a,b,c,d.

Ca-leach curves and calcium concentrations for broken pieces in the closed systems: after hardning without CO_2 access (a,b), and after drying and CO_2 exposure (c,d).

Fig. 14 a,b,c,d.

Cs and Sr leach curves, Sr-concentrations and pH development for closed systems with broken pieces pre-dried and exposed to CO_2.

5.3. Inactive spherical samples.

In addition to the leaching experiments described above experiments have also been made to compare the behaviour of the GEODUR products when exposed to ordinary leaching (with CO_2 access) and to dry/wet cycling.

Two spherical samples (d=4.7 cm) were cast in rubber moulds from each of the inactive GEODUR products type 1, 2 and 3. The samples were fitted with a stainless steel wire as handle so that they could be weighed freely suspended in air as well as in water, see Fig. 15.

After hardening (35 days) both set of sample were first immersed in M = 170 ml water. They were then left standing at 20°C for 8 days whereafter the systems were weighed and water loss due to evaporation compensated by adding about 20 ml fresh water. The spheres were then taken up and weighed rapidly in air after removal (filterpaper) of droplets on the surface. They were transfered to a new beaker with 170 ml deionized water (of the same temperature as the sample) and weighed suspended in this nearly pure water. The pH of the leach water in the original beaker was measaured and the solution acidified (so that any precipitates of $CaCO_3$ on the beaker were dissolved) before analyses for Ca and Na.

The spheres were then leached again for 8 days before the procedure was repeated. This treatment - except that the length of the leach period was extended to 14 days - has been continued for 126 days with one set of the samples.

The other set of spheres was only immersed in water during every second 14 days' period. In the intervening periods the samples were left hanging in the laboratory atmosphere so that partial drying took place. This dry/wet cycling is a rather severe treatment likely to influence the volume stability as well as the leaching behaviour of the samples.

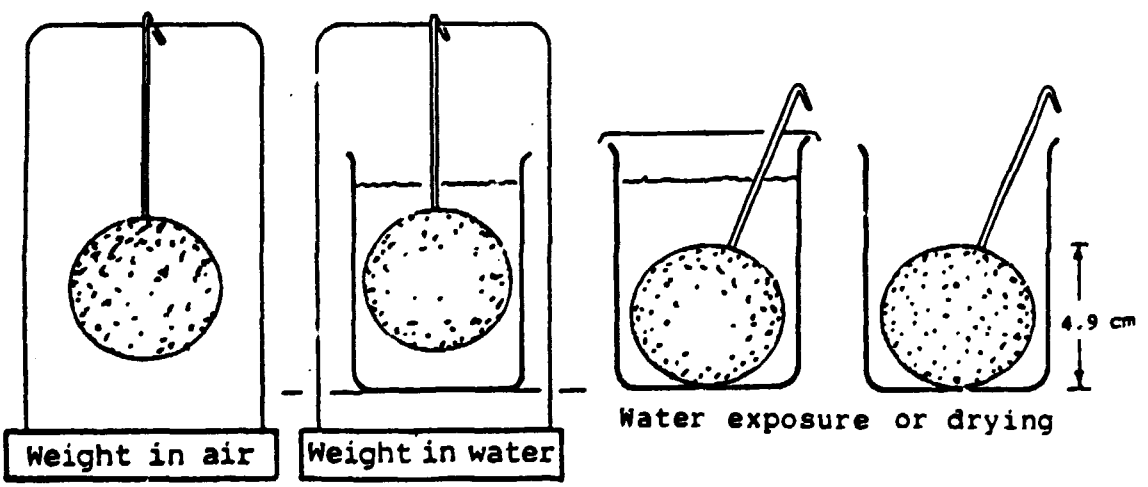


Fig. 15. Weighing procedure and storage conditions during water exposure or drying of spherical samples of cemented soil.

Using the Archimedes principle the change in density with time and exposure can be calculated from the weight measurements. It is also possible to determine even quite small volume changes which may be the first indications of physical damage to the samples. In combination with corrections for leached material (assumed to be $Ca(OH)_2$) the weight measurements also give the water uptake in the material. However, in these open systems reaction with CO_2 from the atmosphere will result in some precipitation of $CaCO_3$ in the pore system of the sample. Correction for the CO_2 uptake is difficult to make, and the calculated water uptake will therefore be somewhat overestimated.

The Na- and Ca-leach curves are shown in Figs. 16a,b and 18a,b. The leached fraction are given as % on the left-hand scale and the equivalent leached thickness in mm on the right-hand scale. The calculated thickness is based on the surface area of the sphere and this approach is only reasonably correct when the leached layer is thin compared with the dimensions of the samples. For Ca this may be permissible although Ca bound in different minerals may leach differently. However, if the spherical geometry was influencing the Ca leaching it would result in downward bending leach curves, and that is not the case.

Na is leached to above 100 % indicating that the Na concentrations given in Table 3 are too low. One possible source could be degradation of Na-containing feldspar in the soil in the strongly alkaline and Ca-rich environment in the products. Disregarding an initial surface effect the Na-leach curves are also nearly linear when plotted against the square root of time, indicating that leaching has not penetrated too far into the sample.

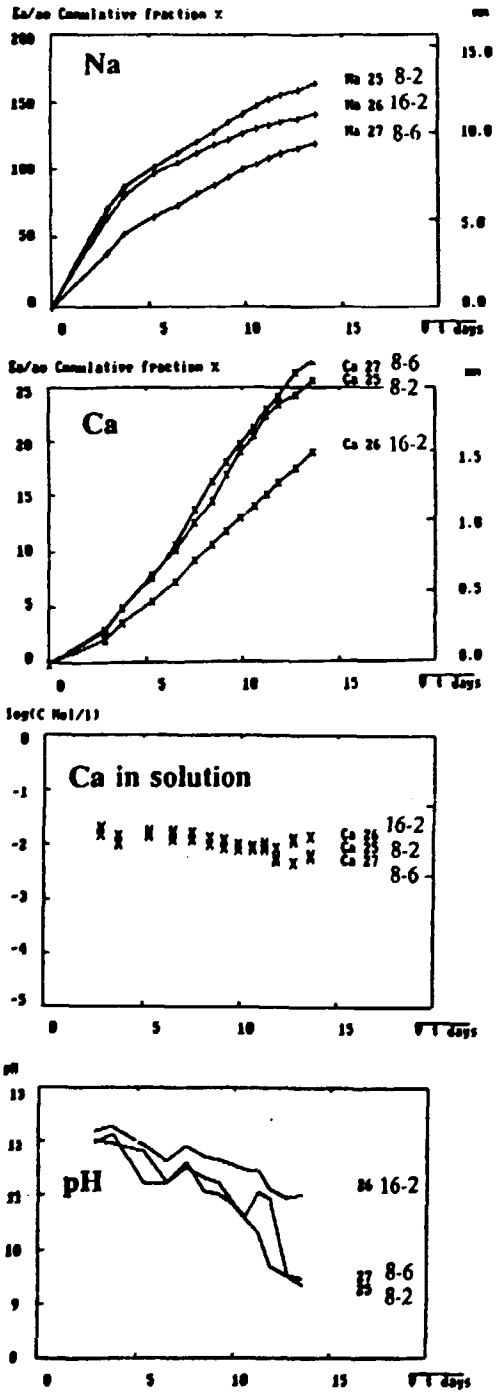
When exposed to wet/dry cycling the leaching of Ca as well as Na is decreased. The exposure-time to water for these samples is only half of the time the permermanently immersed samples are leached: the horizontal part of the leach curves represents the drying periods. Carbonation has probably penetrated to a greater depth during the dry periods. The uncertainties about availability of Na and Ca for leaching under these circumstances makes it impossible to say whether movement of soluble salts towards the surface during the drying periods is contributing significantly to the release, but such a mechanism could well be important for some elements or components.

The Ca 'concentrations' (after acidification) are shown in Figs. 16c and 18c. Much of the calcium was present as calcium carbonate precipitates on the wall of the beakers. The pH measurements are recorded in Figs. 16d and 18d. It is obvious from these curves that the carbon dioxide has influenced the samples under wet/dry cycling much more than the permanently immersed: The pH has dropped from 11 to about 8 and the amounts of leached Ca is much decreased.

The results from the weight-change measurements are shown in Figs. 17 and 19.

Some water is taken up into the permanently immersed samples, see Fig. 17a. Taking the product density into account the amounts are 0.02 and 0.05 g/g product or about 0.2 to 0.3 g water/g cement in the products. It is possible that some of the water is consumed by delayed hydration reactions, but most is probably taken up by a more complete water filling of the pores. The slight swelling: 0.1 to 0.25% (Fig. 17c) accounts for only about 20% of the water uptake.

Spherical samples, permanently immersed exposed to CO_2



Figs. 16abcd.
Fractions of Na and Ca leached from spherical samples of three types of cemented soil continously immersed in water.
The Ca concentration and the pH of the leach water are also given.

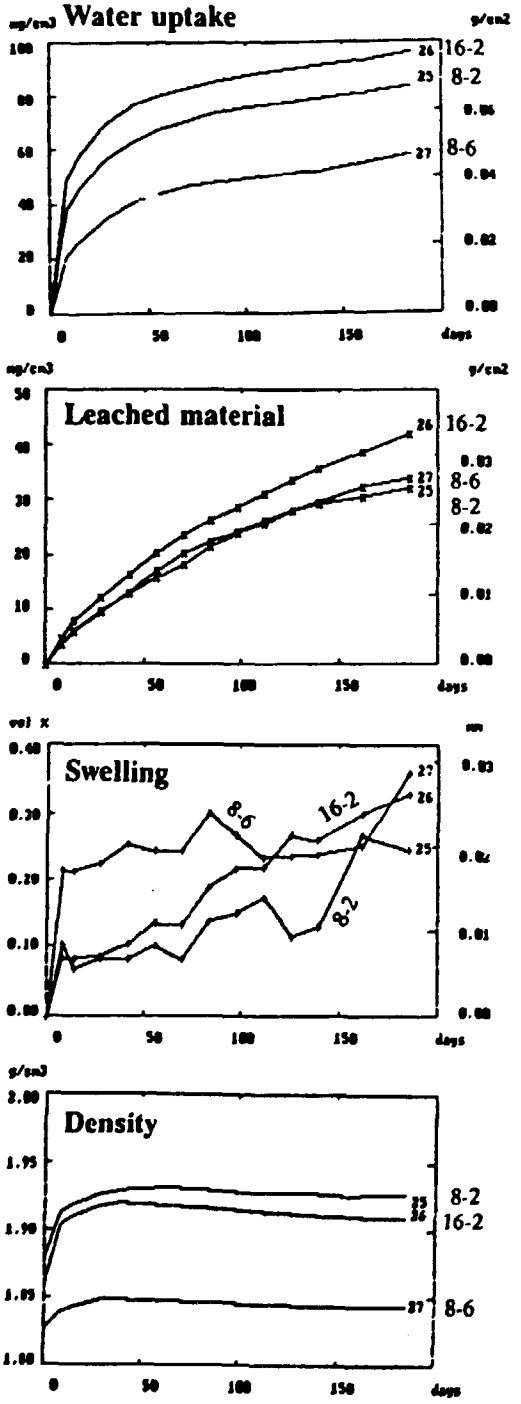
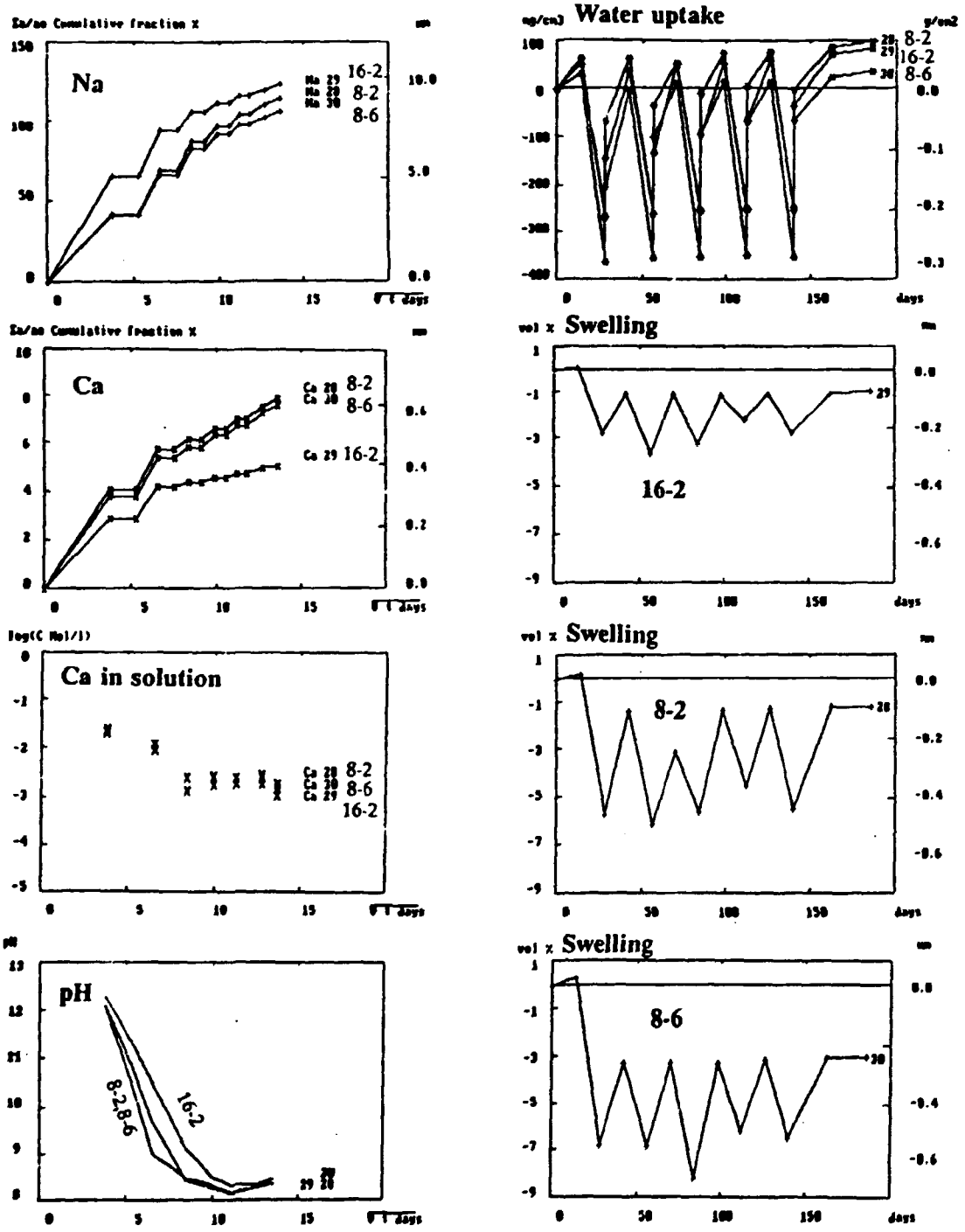


Fig. 17abcd.
The water uptake, swelling and the apparent density of the spherical samples during immersion in water.

Spherical samples, wet/dry cycling exposed to CO_2



Figs. 18abcd.
Fractions of Na and Ca leached from spherical samples of three types of cemented soil exposed to wet/dry cycling.
The Ca concentrations and the pH of the leach water are also given.

Figs. 19abcd.
The water uptake and the swelling of the three spherical samples during wet/dry cycling.
The prolonged period of water immersion at the end of the experiment did not result in reswelling to the original volume.

The water uptake, the swelling and the leaching are also reflected in the sample densities shown in Fig. 17d. The maximum densities were reached after 30 to 60 days of immersion.

In case of the samples exposed to dry/wet cycling the behaviour is quite different. The water uptake varies between 0.02 and - 0.15 to - 0.20 g/g product i.e. most of the free pore water (see table 6) is lost during the drying part of the cycle but is recovered again when the samples are reimmersed. The volume variations associated with the cycling is considerable as illustrated by Figs. 19bcd for the three samples. For the materials with 8% cement the contraction on drying is about 6 to 8 vol% and for the 16% material the contraction is about 3 vol%. The swelling after reimmersion does only partly compensate for the contraction. No visible sign of damage (cracks etc.) to the samples was observed. The high degree of contraction as well as the ability to accomodate the large volume changes must be ascribed to the large content of clay in the soil.

6. Diffusion cell experiments.

6.1. Diffusion of TOH and ^{134}Cs through water-saturated cemented soil.

If cement solidified soil is used as barrier material around e.g. more strongly contaminated soil - which is one option for the use of cement stabilized soil - the rate of diffusion through an original slab of the solidified soil is of more relevance than the leaching results obtained in Section 5.1.

It has been shown previously /5,7/ that the effective diffusion coefficients describing migration through a slab may not necessarily be identical with the diffusion coefficients obtained from leaching experiments. Furthermore two types of diffusion coefficient may may be defined to account for transport through a slab of porous materials. One is the diffusive permeablity P and the other the effective diffusion coefficient $D_{e(slab)}$ for transport through individual pore channels. The relationship is $P = S \cdot D_{e(slab)}$ where S can be regarded as the fraction of the sample's cross-sectional area available for transport.

$D_{e(slab)}$ is obtained from the formula:

$$D_{e(slab)} = x^2/(6 \cdot \lambda)$$

where x is the sample thickness and λ is the time lag.

P is a more direct measure for the rate of transport through the slab and is therefore often reported as the diffusivity for the material. It is given directly by the slope α of the break-through curve according to Fick's first law applied on the slab regarded as an ideal membrane:

$$P = \alpha \cdot c \cdot x/\Delta c$$

where c is the concentration at the strong side and $\Delta c/x$ the concentration gradient over the slab. For further theoretical considerations see /7/.

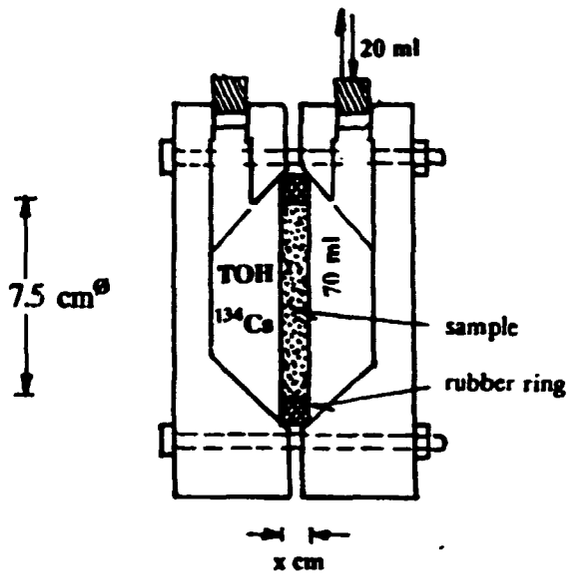


Fig. 20. Diffusion cell used for experiments with migration of tritiated water (TOH) and $^{134}Cs^{+}$ through slabs of cemented soil.

Three 2 cm thick slabs made from the 8-2, the 8-6 and the 16-2 materials and tested for macro defects by measurement of the hydraulic conductivities (Section 4.1) were mounted in diffusion cells as shown in Fig. 20 with a solution containing tritiated water (TOH) and $^{134}Cs^{+}$ on one side and 'pure' water on the other. The solution on the weak side was sampled regularily and analysed for tritium by liquid scintillation counting and for Cs by γ-spectroscopy.

The results are shown in Figs. 21ab as the amount of strong solution which should have passed through each cm^2 slab area to account for the activity found in the samples of weak solution.

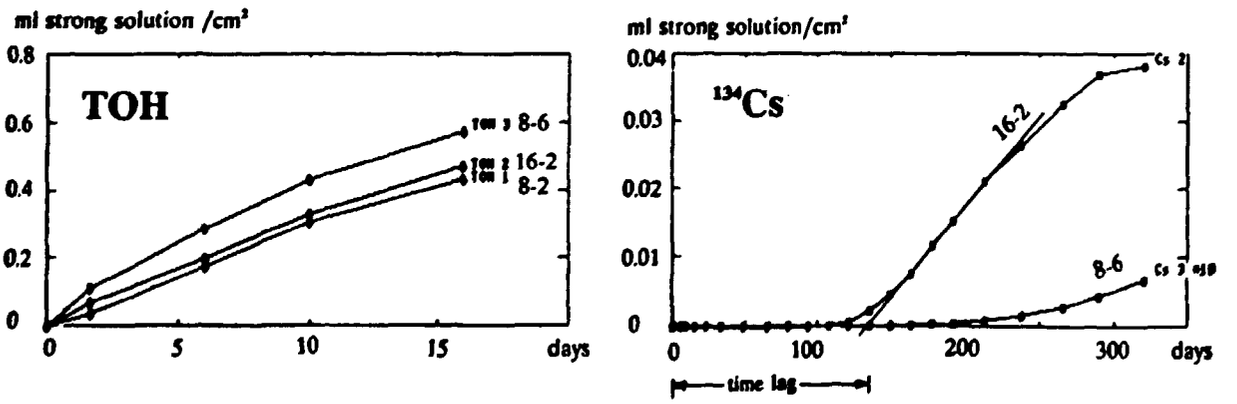


Fig. 21ab. Results from experiments with migration of tritiated water and $^{134}Cs^{+}$ through slabs of cemented soil.

Table 9. Diffusion coefficients obtained from time lags and diffusive permeabilities for the migration of $^{134}Cs^+$ and tritiated water through ~2 cm thick slabs of cemented soil.

Product type:		8-2	16-2	8-6	Product a w/c=0.45 (ordinary concrete)
Sample thickness: cm		2.05	2.01	2.05	~1.0
Cs					
$D_{e(slab)}$	cm^2/sec	$<20 \cdot 10^{-9}$	$61 \cdot 10^{-9}$	$36 \cdot 10^{-9}$	$76 \cdot 10^{-9}$
P	cm^2/sec	-	$5.5 \cdot 10^{-9}$	$0.2 \cdot 10^{-9}$	$3.7 \cdot 10^{-9}$
$D_{e(leach)}$*	cm^2/sec	$0.1 \cdot 10^{-9}$	$0.35 \cdot 10^{-9}$	$0.01 \cdot 10^{-9}$	$50 \cdot 10^{-9}$
$R = D_{e(slab)}/D_{e(leach)}$		<200	170	~300	1.5
TOH					
P	cm^2/sec	$870 \cdot 10^{-9}$	$880 \cdot 10^{-9}$	$1140 \cdot 10^{-9}$	$26 \cdot 10^{-9}$

* values taken from Table 7.

The break-through of TOH was extremely fast and no time lag could be be determined. Approximate values for P are given in Table 9. They are considerably higher than for ordinary concrete (product a) reflecting the high degree of porosity in the cemented soil.

On the other hand the break-through of Cs was slow and has in fact not yet occured for after ~300 days for the sample of the 8-2 material. $D_{e(slab)}$ and P values for the 16-2 and 8-6 material are given in Table 9. They are rather similar to the ones obtained for the ordinary construction concrete although the P values tend to be lower for the low-cement material. This is in agreement with the tendencies found in the leaching experiments. The high values for the ratio $R = D_{e(slab)}/D_{e(leach)}$ indicated a high degree of tortuosity of the pore structure in the cemented clayey soil /7/.

The experiments have only been done with three samples, one of each material, and since the diffusive transport through slabs may be influenced rather drastically by minor defects in the slabs the results should not be stressed too far.

However, it is probably permissible to conclude that the cemented soil is as good as ordinary concrete to prevent Cs migration when used as barrier around disposed waste materials. This does not preclude that clayey soil without cement would perform even better as a barrier for Cs.

Sr migration through slabs was not investigated. From the leaching experiments one would expect rather rapid transport in a CO_2-free environment but slow, if any, transport in the cementitious materials when placed in more ordinary situations with CO_2-access.

6.2. Diffusion of water vapour through (partly) dry cemented soil.

As a supplement to the other pore structure-related properties the rate of water-vapour diffusion through slabs of (partially) dry cemented soil was also determined using a simple weighing technique: One or two ~4 cm thick slabs of the 8-2, 8-6 and 16-2 materials were mounted in the top of cut polyethylene bottles containing some concentrated sulfuric acid at the bottom, ~RH=0. The systems were stored in glass jars with some weak NaOH solution present to ensure an outer ~95% relative humidity CO_2-free atmosphere. The weight increases due to the vater-vapour migration through the slabs were then followed for ~100 days. Using a modified mounting technique the vapour migration through ~2 cm thick layers of the clayey soil without cement could also be measured.

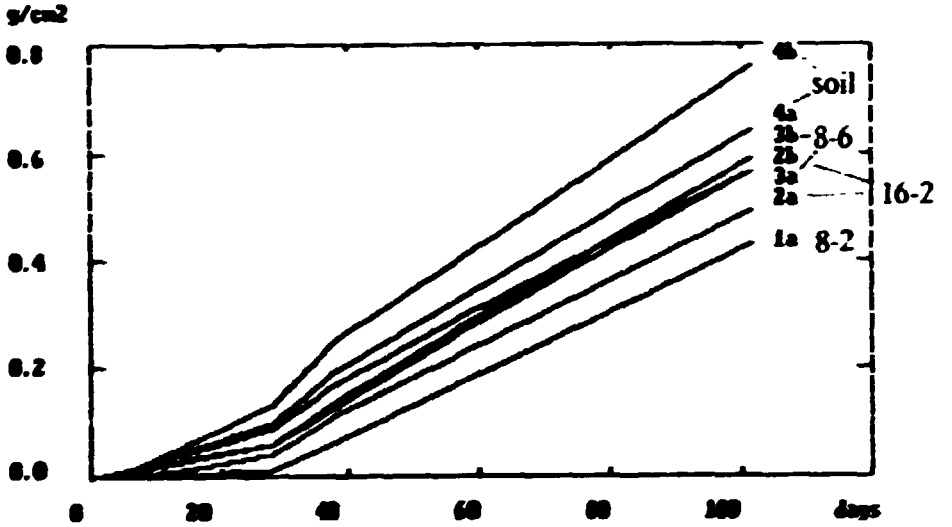


Fig. 22. Weight increases as function of time for five systems with ~4 cm thick samples of cemented soil and two with ~2 cm thick samples of rammed clayey soil without cement when stored with a relative humidity gradient of 95 % over the slabs.

The results are shown in Fig. 22. The diffusive permeability P_v can be calculated from the slope α of the curves according to the formula:

$$P_v = \alpha \cdot x/(p_1-p_2)$$

where x is the thickness of the slab and p_1 and p_2 are the partial vapour pressures at the two sides /7/. The values are given in Table 10. It is seen that there is nearly no difference between the three types of cemented soil, that the soil itself is somewhat less permeable (due to the lower initial water content) and that of an ordinary construction concrete is even less permeable. The high porosity of the cemented soil is no doubt the explanation for the high diffusivities for water vapour in the partially dried samples.

Table 10. Water vapour diffusivities in partially dry slabs of cemented soil and rammed soil without cement. (The codes gives % cement - % GEODUR sol. - % original water in sample.)

Product type:	8-2-24	16-2-24	8-6-25	0-0-14 (soil without cement)	Product a (ordinary concrete)
P_v cm^2/sec	0.019	0.021 0.020	0.022 0.013	0.013 0.013	0.005 0.003

7. Supplementary investigation.

In the description /3/ of the Nordic KAN 2 project it is mentioned that sludges from ordinary waste water purification plants could be a problem material in connection with major nuclear accidents.

A few tentative experiments have been made to see if cement + GEODUR solidification is a possibility. However, the results were not promising.

Anaerobic stabilized and partly dewatered sludge from the waste water purification plant at Risø was used. The water content was about 57.4 % and the ash content about 63.6 % of the dry material.

The mixtures given in Table 11 were prepared, they could all be cast but did not solidify. Even after 4 months they are still quite soft like clay paste. With sewage sludge the GEODUR additive may not be able to prevent the retardation of the cement reactions, but the reason for the lack of hardening could also be the very high water content necessary to make a castable mixture from the sludge. The water-binding ability of the sewage sludge is even higher than for the clayey soil used in the other experiments.

An experiment (SJ1) with sludge mixed with a moderate amount of soil gave no significant improvements. However, additional experiments could be done with (much) higher soil/sludge ratios, somewhat increased cement contents, and maybe decreased water contents, even if this results in non-castable products like No. 5 in Table 3.

Pre-drying of the sludge was shown to be of no particular value before cementation. Incineration is of course a posibility, and no doubt the ashes from such a treatment can easily be cement-solidified with (or without) the GEODUR addtive.

Table 11. Mixtures prepared to investigate whether sewage sludge can be solidified using the GEODUR process.

Recipes g							In products			
	Sludge	Soil	Geodur	SRPC	Water extra	Water total	% dry material from:			%
With dry materials:	42.6%	91.2%	1%	~100%			Sludge	Soil	Cement	Water
SS1	1500	-	30	120	200	1090	34.5	-	6.5	59
SS2	2000	-	80	320	400	1630	30.4	-	8.3	58
SJ1	2000	1000	50	200	600	1890	22.1	23.7	5.2	49
Sa2	2350	-	47	188	-	1390	38.4	-	7.2	54

8. Summary and recommendations.

Various experiments have been made in a first attempt to document the possible advantages of using the GEODUR process for cement solidification of soil as a waste management method for soil contaminated with radioisotopes.

A clayey top soil from the Risø area was used in combination with 8 % or 16 % sulphate resistant Portland cement and 2 or 6 % of the GEODUR additive (as a 1 % solution). The hardening proceded satisfactorily. Samples without the additive were also prepared.

The GEODUR products were not particularily strong (compression strength ~5-10% of normal construction concrete) but still acceptable as solidified waste in waste packages and probably also as backfill or for sub-surface construction of barriers surrounding more heavily contaminated materials.

Due to the clayey soil a high water content (~24%) was necessary to obtain mixtures which could be vibration cast. In combination with the low cement content this resulted in high w/c ratios (~4) and rather high porosities: about 25-30 vol% in the products. Lower porosities can be obtained if it is acceptable to use drier mixtures which must be rammed in place.

Although the porosities are high the hydraulic conductivities are still quite low: of the same order as for normal construction concrete. This is important if the material is to be used in barrier construction.

Diffusive transport of tritated water through slabs of the materials was quite fast as could be expected for such high-porosity products. The permeability for water vapour in the partially dry materials was also high.

Diffusive transport of Cs-ions through slabs of the materials reflects some of the same chemistry as described below. The cemented soils are probably as good as ordinary construction concrete when used as barriers, but soil without cement may well be better.

The leaching properties are complicated:

Cesium is only slightly leached, in fact much less than it would have been from an ordinary cemented waste material. This is no doubt due to the retention properties of the clay in the soil. The Cs-leaching was higher for the product with 16 % cement than for the ones with 8 %. It was later demonstrated /8/ that leaching is even lower from the soil as such without any mixing with cement. The reason is probably the increased concentration of ions competing about the exchange sites on the clay in the cement-containing materials. The Cs release was further enhanced by leaching in 3 % NaCl solution while access to CO_2 from the atmosphere had no particular influence. Pre-drying of the materials before exposure to water resulted in an important decrease in the Cs release especially for the 16 % cement material.

Strontium shows a completely different behaviour and is leached much more rapidly from the cemented soil materials than cesium. Furthermore, there is a strong difference between Sr-leaching in the systems with CO_2 access and in those without. When carbonation of the sample surface has taken place the Sr-release is decreased strongly. The effect is also obtained when the carbonation is due to contact with the atmosphere before exposure to water.

The Sr-leaching (with or without CO_2 access) is slightly higher in 3 % NaCl solution than in deionized water and there is - especially for the NaCl systems - a tendency to renewed increase in Sr leaching when the pH has decreased sufficiently due to CO_2 uptake.

Also calcium is leached quite easily by diffusion from these porous samples. This is important since the extensive Ca-leaching in the long run will result in decreased pH within the samples and even in some loss of mechanical strength. Reaction with CO_2 proceeds rapidly in the very porous materials and will also reduce the pH of the pore water.

As far as Zn-leaching is concerned the information obtained is meagre since ^{65}Zn could not be detected in any of the water samples. However, in some ways this is positive since it demonstrates that the leach rate is extremely low, and apparently remains so even for the samples which are leached to a considerable degree for calcium, etc.

In summary the following conclusions are drawn from the experiments:

- Monolithic non-dusting cement-solidified soil can be produced from clayey top soil using the GEODUR process.
- The products prepared from clayey soil have low hydraulic conductivities.
- They are reasonably volume stable when immersed in water but contracts 3-8 vol% when dried.
- Due to the high porosity diffusion-controlled processes tend to proceed rapidly.
- Leaching is therefore also rapid unless ion-exchange or precipitation reactions inside the pore structure minimize the release.
- This is apparently the case for Cs (good) and Zn (very good), but not for Sr or Ca.
- If the product - as would be the case in many practical applications - reacts with carbon dioxide from the environment a satisfactorily behaviour for Sr may still be attained.
- Extensive carbonation may possibly have negative effects on other properties of the products, but none have so far been encountered.
- From comparison with later experiments /8/ it appears that no improvement of the retention of Cs and Sr is obtained by the cementation process compared with retention in the untreated soil.

Recommendations for further work:

It is an open question if and how much safety improvement is gained by use of the GEODUR process compared with storage or disposal of the contaminated soil as such. Both methods may be perfectly acceptable, but the additional effort of the mixing involved in the GEODUR process (or any other conditioning) must be motivated by a reasonable safety gain.

In the case of the ^{90}Sr-contaminated soil in storage at Risø (see Introduction) the main advantage would be conversion into monolithic units of a non-dusting material. It is questionable whether this in itself would be worth the trouble and the exposure risks during processing. A minimum requirement would be that it is demonstrated on a larger scale, and preferably with samples of the actual soil, that carbonation really is able to ensure a good fixation of the isotope in the material.

For the Nordic studies of accident-related handling and disposal of contaminated soil, Cs-isotopes and not so much strontium will be the important pollutant. Here the preliminary results with the Risø soil are not too promising. Additional experiments with other soil types are absolutely necessary. Both the retention properties and the water requirements for making castable mixtures are likely to be much dependent on the soil type. No major loss and preferably an improvement in retention capability for Cs must be demonstrated for at least some common soil types. The influence of drying and ageing of the products should be investigated.

Another line of investigation could the possibility of using low water-containing, non-castable mixtures which can be rammed in place e.g. with road construction equipment.

A third line of investigation would be further studies on solidification of sewage sludge and/or various ashes for example from combustion of contaminated peat.

As far as heavy metal contaminated soil is concerned the lack of measureable leaching of Zn is very promising. However, studies of the directly relevant pollutants (Cd, Pb, Hg, As . .) should of course be made. In this context it is important to follow the leaching behaviour for a sufficently long time so that the releases also are documented for the long-term situation where extensive loss of calcium may have occured together with pH changes and/or carbonation.

In this context also some heavy radioisotopes may be of interest: for example in waste from uranium mining and milling or possibly in contaminated soil found in connection with decommissioning of other nuclear installations.

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CHARACTERIZATION OF WASTE PRODUCTS PREPARED FROM RADIOACTIVE CONTAMINATED CLAYEY SOIL CEMENTED ACCORDING TO THE GEODUR PROCESS

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Date November 1990

Department or group
NUK (BEH)

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Abstract (Max. 2000 char.)

Abstract: Radioactive contaminated soil may arise due to accidents of various types or may be detected during decommisioning of nuclear installations. Ordinary surface soil cannot normally be conditioned using conventional cementation processes since the content of humic materials retards or prevents the solidification. An additive available from the Danish firm Geodur A/S makes it possible to circumvent this difficulty and to produce a monolithic, nondusting waste type using rather small amounts of cement. The report describes work on characterization of such a cemented waste product prepared on basis of a clayey top soil from the Risø area.

The claimed advantages of the process was verified, and data for the compression strength (low), hydraulic conductivity (satisfactory) and other pore structure-related properties are given for the obtained products.

Unfortunately the behaviour of cesium and strontium, representing two of the most relevant radionuclides, was not too promising.

The retention of cesium is satisfactory, but less good than for the untreated soil. Greatly improved cesium retention after drying of the materials was noticed. Good retention of strontium is only obtained after reaction of the material with carbon dioxide from the atmosphere. The behaviour of the two isotopes in other types of cemented waste is somewhat similar, but the decrease in retention compared with untreated soil makes the process less interesting as a possibility for remedial actions after accidents, etc. Some further studies of the cemented soil waste are beeing made within the frame of the Nordic Nuclear Safety Studies.

Elements forming low solublity components in the high pH environment in the cemented soil will probably be retained quite efficiently. This was demonstrated in case of Zn.

Descriptors - INIS

ADDITIVES; CALCIUM; CARBON DIOXIDE; CEMENTS; CESIUM ISOTOPES; CLAYS; DIFFUSION; HARDENING; LEACHING; MECHANICAL PROPERTIES; POROSITY; RADIOACTIVE WASTE PROCESSING; SOILS; SOLIDIFICATION; STRONTIUM ISOTOPES; WATER; ZINC

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